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USAFOEHL REPORT

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# Design Criteria for Process Wastewater Pretreatment Facilities

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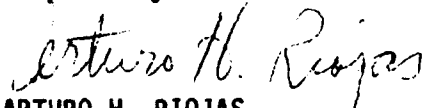
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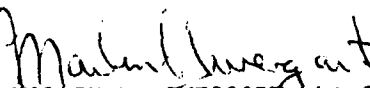This report has been reviewed and is approved for publication.

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Many industrial wastewater streams can be discharged into Publicly Owned Treatment Works (POTW); however, they must meet prescribed characteristics, and concentrations of specific contaminants must not be exceeded. Wastewater sources on Air Force bases and the corresponding wastewater characteristics are described, applicable discharge limits are reviewed, and typical pretreatment process sequences which would be effective in bringing these wastewater streams into compliance with the relevant discharge limits are given for the wastewater classes identified in the report. A description of wastewater treatment processes is included, and design equations and procedures for the processes are provided in the appendixes.

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# ILLUSTRATIONS

# I. INTRODUCTION

Purpose: The purpose of this report is to provide design criteria for pretreatment needs for discharge of industrial wastewater streams to Publicly Owned Treatment Works (POTW).

Problem: The provisions of the Resource Conservation and Recovery Act (RCRA) and the National Pretreatment Standards prohibit the discharge of hazardous waste or waste which will inhibit downstream treatment processes. Some effluent limitations have been discussed previously (letter from USAFOEHL/CV to HQ USAF/SGES on Criteria for Industrial Wastewater Effluent dated 26 Dec 1984).

Scope: This report reviews available options and design criteria for pretreatment of base-generated wastewater streams but does not determine preferred treatment processes. Typical waste stream compositions are included. Optimum process configuration will be site-specific.

The scope of this report is limited to published literature and data, and the results of wastewater characterization surveys published as USAFOEHL Reports. No pilot plant studies have been conducted.

# II. DISCUSSION

This section contains a discussion on the sources of wastewater streams discharged from Air Force bases, pollutant discharge limits, and alternative treatment processes available to bring effluent streams into compliance with discharge limits.

A. Wastewater Types, Sources, and Pollutant Concentrations

The types and volumes of liquid wastes generated depend on the operations conducted at the Air Force base. Not all processes discussed are present on all bases. Although overall base discharge flows are relatively stable, many wastewater streams are generated by batch processes, making effluent pollutant concentrations subject to wide fluctuation.

Wastewater streams can be categorized into one of the classes listed in Table 1.

## Table 1
## WASTE STREAM CLASSIFICATION

| Class | Wastewater Description |
|-------|------------------------|
| 1 | Streams containing high concentrations of "nontoxic" organics (e.g., washrack aqueous effluent). |
| 2 | Streams containing high concentrations of organics, some of which may be classified as "toxic," and low concentrations of heavy metals (e.g., paint stripping wastewater). |
| 3 | Streams containing trace levels of "toxic organics" (e.g., degreasing solution rinses from engine cleaning). |
| 4 | Streams containing heavy metals and low or no organics (e.g., plating rinse water, neutralized battery acid). |
| 5 | Streams containing cyanide and low concentrations of heavy metals and some organics (e.g., from metal plating or photo lab). |
| 6 | Streams containing cyanide, heavy metals, and low or no organics (e.g., wastewater containing dilute amounts of Alodine solution). |

The advantages and disadvantages of pretreating individual streams prior to discharge will be discussed later in this report. The major sources of wastewater are reviewed below and corresponding typical concentration ranges are listed. Comparable wastewater characterizations for streams generated by industry in the private sector can be obtained in the EPA Treatability Manual, Vol II. (USEPA, 1980b).

### 1. Washracks

Wastewater streams generated at aircraft washracks may be hot (150-180° F) and contain oil and grease from aircraft engines and bearings. Organic detergents which contain materials such as alkyl phenol ethoxylate, Stoddard Solvent, monyl phenol polyethylene glycol, sodium dodecyl benzene sulfonate, ethylene glycol monobutyl ether, and butyl cellosolve are used in washrack operations and add to the chemical oxygen demand (COD) of the wastewater. Residual paint and paint stripper from aircraft stripping operations may be removed with water at the washracks.

Cadmium levels, however, may be higher than would be expected from paint stripping residue alone. Cadmium can usually be detected wherever zinc is present. Paint can be removed from aircraft surfaces accidentally by the abrasive action of high pressure water streams. Some paint primers contain zinc chromate, and, therefore, can contribute to the cadmium levels found in washrack wastewater.

In addition, soft metals such as brass, consisting of about one-third zinc, are susceptible to chelation by some detergents. Storage tanks, pumps, or any dispensing equipment containing brass in contact with alkaline detergents could become additional sources of cadmium, copper, and zinc.

Wastewater streams from aircraft washracks are considered Class 1 unless aircraft surface contamination contains paint stripping residue, in which case they become Class 2 streams. Typical ranges of relevant contaminant concentrations for aircraft washrack wastewater are given in Table 2.

## Table 2
## AIRCRAFT WASHRACK WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) |
| --- | --- |
| BOD* | 100-2500 |
| COD* | 700-2500 |
| TOC* | 130-1200 |
| Oil and Grease | 2-55 |
| Cadmium | 0-0.2 |
| Chromium (total) | 0-4 |
| Phenol | 0-210 |
| Methylene Chloride | Trace |
| Surfactants | 0-2 |
| Ammonia Nitrogen | 80 |
| Suspended Solids | 50-90 |

*BOD = Biochemical Oxygen Demand, COD = Chemical Oxygen Demand, TOC = Total Organic Carbon

Motor pool washrack wastewater (Class 1) is similar to that generated at aircraft washracks with two exceptions: (1) it is generally not hot, and (2) it does not contain paint and stripper residues. Typical ranges of relevant contaminants in mg/l for motor pool washrack wastewater (Chian et al., 1974) are given in Table 3.

## Table 3
## MOTORPOOL WASHRACK WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) |
|---|---|
| Total Solids | 570-12,900 |
| COD | 64-3,400 |
| TOC | 24-1,700 |
| Oil and Grease | 20-8,700 |
| Surfactants | 0-2 |

2. Battery Shop

Wastewater from the battery shop is generated from the neutralization and dilution of lead-sulfuric acid battery solution. The battery acid solution is neutralized with sodium bicarbonate, generating a Class 4 wastewater stream. Typical relevant contaminant concentrations (samples taken at Dover AFB in Feb, Mar 1986) are given in Table 4.

## Table 4
## BATTERY SHOP WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) |
|---|---|
| Lead | 14.9 |
| pH | 7.5* |
| Copper | 3.4 |
| Iron | 15.0 |
| Zinc | 21.5 |

*pH units rather than mg/l

3. Paint Stripping

Wastewater from paint stripping (class 2) contains chromium and solvents with high COD concentrations. Two types of paint strippers are commonly used: phenolic and non-phenolic. Phenolic paint strippers usually contain phenol, methylene chloride and sodium chromate. Non-phenolic paint strippers usually contain methylene chloride and ammonium hydroxide, and are usually used in conjunction with ethanol or methyl ethyl ketone (MEK).

Methylene chloride comprises the largest solvent volume fraction in both phenolic and non-phenolic paint strippers. Although methylene chloride is highly volatile (vapor pressure of 400 mm Hg at 24.1°C, Perry and Chilton, 1973), its solubility in water, 13.2 g/l at 25.0°C (Mellan, 1957), is also high, making it a significant contaminant in the wastewater. Typical ranges of relevant contaminant concentrations for paint stripping wastewater (Perrotti, 1975; samples from Randolph AFB, Sep 1986, and Kelly AFB, Apr 1987) are given in Table 5. Low concentrations of cadmium are often found in wastewater from paint stripping operations. Cadmium is associated with zinc and is usually detected whenever zinc is found. Zinc chromate coatings (to inhibit corrosion) which are stripped with paint strippers will contain some cadmium.

### Table 5
### PAINT STRIPPING WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) | |
| --- | --- | --- |
| | Phenolic | Non-phenolic |
| pH | 8.0-8.6* | 9.6* |
| Chromium | 17.5-200 | 30 |
| Cadmium | 0-0.38** | 0-0.38** |
| Ammonia | - | 160 |
| Methylene chloride | 100-3,000 | 13.4-51.4 |
| Phenol | 1,000-4,000 | - |
| Oil and grease | 8-2,000 | - |
| COD | 5,000-36,000 | 8,500 |
| Total suspended solids | 100-1,000 | 90 |
| Total solids | 800-4,000 | 5,200 |

*pH units rather than mg/l
**Cadmium concentration depends on the aircraft paint system and parts being stripped.

## 4. Paint Shop

Paint removers containing glycol ethers, methyl ethyl ketone (MEK), toluene and xylenes, and paint thinners containing nitrocellulose and cellulose acetate are commonly used. Paint, thinners, and removers should not reach the sewer directly; however, the recirculating pine-soap solution in the "waterfall" vent scrubbers which may contain some of these materials may be periodically discharged to the sewer. Fine aerosol mist from the spray painting process and volatile solvents find their way into the scrubber solution and, therefore, into the sewer. Characteristics and concentrations for relevant materials (samples taken at Randolph AFB on 21 Nov 1985) are given in Table 6.

**Table 6**
**PAINT SHOP VENT SCRUBBER WASTEWATER**
**CONTAMINANT CONCENTRATIONS**

| Pollutant or Property | Concentration (mg/l) |
|---|---|
| COD | 760 |
| $BOD_5$ | 720 |
| TOC | 150 |
| Suspended Solids | 40 |
| Lead | 0.03 |
| Chromium | 1.4 |

5. Engine Cleaning

A series of baths is used to remove all traces of fuel, oil, and grease in the process of cleaning an engine or engine parts for repairs or inspection. Drag-out (entrained solution) from parts is collected and returned to the baths. Baths are removed periodically by truck or drummed. Rinse waters for parts emerging from the various baths are the potential pollution sources.

Sodium or potassium permanganate baths are a potential source of manganese contamination. Drag-out from the permanganate baths, which contain 7-10 oz. of potassium permanganate per gallon, is diluted with water in the rinse tanks. The rinse water leaving the tanks (class 4) typically contains 8-100 mg $KMnO_4$/l and has a purple tint (Herrin, 1986). However, the permanganate is readily reduced by other contaminants in the sewer system and is generally not a concern.

Perchloroethylene (tetrachloroethylene) and 1,1,1-trichloroethane are used as degreasers in engine cleaning operations. They are slightly soluble in water (400 mg/l and 4800 mg/l at 25°C, respectively; Mellan, 1957). These solvents do not find their way into the rinse water directly. Low concentrations are typically found in the monoethanolamine (MEA) bath which immediately follows the solvent baths (with no rinse step between baths).

MEA, used as a carbon remover, is water soluble. Upon MEA degradation, rinse solutions can be a source of ammonia to receiving bodies of water. The dilute concentrations found in rinse water are not likely to present a problem with regard to ammonia nitrogen. The rinse solution from the MEA bath will contain trace concentrations of perchloroethylene and 1,1,1-trichloroethane which contribute to the total toxic organic concentration.

## 6. NDI (Non-Destructive Inspection)

Many engine parts are inspected using NDI penetrant dye techniques following cleaning. As in engine cleaning, the dye solution is applied and drippings are collected for reuse. Rinse water containing residual dye solution is the potential pollution source. Contaminant concentrations in the rinse water depend upon the amount of solution remaining on the parts being inspected and the volume of rinse water used. Dyes typically contain 30-40% xylene (dimethyl benzenes) and ethyl benzene, and have a specific gravity of approximately 1.0. The dyes are typically alkylamino substituted anthriquinones or azo compounds of naphthalene and alcohol. Values of wastewater characteristics that are typical of the NDI process (samples taken from Randolph AFB on 21 Nov 1985) are given in Table 7.

### Table 7
### NDI WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) |
| --- | --- |
| COD | 1510 |
| $BOD_5$ | 1110 |
| Ammonia Nitrogen | 74 |
| Suspended Solids | 560 |

## 7. Photo Lab

Wastewater from photo processing is largely dilute combinations of developer, stopbath and fixer solutions. The three streams are combined and discharged to the sewer with varying amounts of silver being recovered from the fixer solution prior to discharge. The combined discharge is usually rich in acetic acid, has a COD/TOC ratio of about 7, has a low pH, and can contain significant quantities of boron and cyanide. The wastewater could be Class 1, Class 4, Class 5, or some combination thereof, depending on the waste being pumped and the sump size. Photo processing wastewater characteristics and typical ranges of relevant contaminants are presented in Table 8. The ranges were determined from reported photographic waste concentrations (Thomas, J. F. et al., 1974; Newbrough and Kinch, 1981; samples taken at Beale AFB in May and Jun 1985, Randolph AFB on 21 Nov 1985, and Hickam AFB in Jan 1987).

## Table 8
## PHOTO PROCESSING WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) |
|---|---|
| COD | 37-6700 |
| TOC | 5-140 |
| Cyanide | <0.01-12.5 |
| Silver | <0.1-1.11 |
| pH | 4.3-4.4* |
| Boron | 7.0-7.5 |

*pH units rather than mg/l

Special treatment of photographic wastewater for the removal of hydroquinone is sometimes necessary to comply with effluent standards on phenols. Hydroquinone is detected as a phenol (Binovi et al., 1987).

8. Plating Waste

Heavy metals found in plating process wastewater are in dilute concentrations and vary with the type of plating process in use. Cyanides discharged to the sewer are a major concern because of the possibility of the formation and volatilization of hydrogen cyanide. The organic content of wastewater is usually low. Reported process wastewater contaminant concentrations vary greatly between sources. Included in Table 9, are concentration ranges taken from the EPA Treatability Manual, (EPATM) Vol. II (USEPA, 1980b) and ranges typical of summer operations at Kelly AFB (Jun 1986). Numbers in parentheses represent monthly average concentrations.

## Table 9
## METAL PLATING WASTEWATER CONTAMINANT CONCENTRATIONS

| Pollutant or Property | Concentration (mg/l) | |
|---|---|---|
| | EPATM | Kelly AFB |
| TSS* | 0.1-10,000 | - |
| COD | 5-300 | - |
| Cadmium | 0.01-21.6 | 0.05-11.5 (0.8) |
| Chromium | 0.09-530.0 | 0.02-172 (35) |
| Copper | 0.03-270.0 | - |
| Lead | 0.66-25.0 | 0.01-19.8 (0.7) |
| Nickel | 0.02-3,000 | 0.04-120 (3.0) |
| Silver | 0.05-180.0 | - |
| Zinc | 0.11-250.0 | - |
| Cyanide (total) | 0.01-150.0 | 0.05-4.5 (1.0) |

*TSS = Total Suspended Solids

Typically, rinse solutions are trucked away if any of the pollutant concentrations disposal limits are exceeded. For example, disposal limits (in mg/l) of 1.0, 1.0, 0.2, 10.0, and 0.2 might be set for cadmium, chromium, lead, nickel, and cyanide, respectively (Kelly AFB).

### 9. Miscellaneous Contaminants.

Several other chemicals are used at various locations and merit special discussion. When the wastewater produced can be isolated before mixing with other wastewater streams, treatment is usually simpler and more efficient. There are, of course, exceptions to this generalization.

#### a. Alodine Solution.

Alodine solution (an aqueous solution of chromic and other acids) is used at many sites (e.g., tank and radiator shops, paint shops) where, as a corrosion prevention measure, a chromate film is applied before painting metal equipment. The contaminant concentrations in the wastewater depend upon the degree of dilution, with the ratio of cyanide to chromium being approximately 3.6:1. Wastewater containing dilute alodine solution is a Class 6 waste.

#### b. Petroleum Distillates.

Most petroleum distillates are mixtures of hydrocarbon compounds. They are products of specified boiling ranges from distillation columns used to fractionate crude oil and intermediate products from various process units common to the petroleum refining industry. Many distillates have similar boiling ranges. However, they can be distinguished from each

other by the ratios of the various compounds they contain. Normal alkanes comprise a large fraction (over 50%) of Stoddard Solvent, PD-680, and JP-4 Jet Fuel. Normal alkanes are also relatively nonbiodegradable, when compared to the branched alkanes and other distillate components. Pollutant sources can often be determined by establishing the relative concentrations of these compounds. Tables 10, 11, and 12 list compounds that are typically included in the characteristic signatures of Stoddard Solvent, PD-680, and JP-4 Jet Fuel, respectively. The analyses given are not complete. They represent the normalized volume percent of only the compounds listed. Actual concentrations of those compounds may be as low as half the listed values, but the relative concentrations should remain constant.

(1) Stoddard Solvent.

Stoddard Solvent is used as a general-purpose degreasing solvent (also used in the dry cleaning industry). It is relatively insoluble in water and is largely composed of 9-, 10-, and 11-carbon atom normal alkanes. It also contains trace amounts of 7-, 8-, 12-, and 13-carbon atom normal alkanes with as much as 5 vol% aromatics (toluene and xylenes). Wastewaters containing dilute amounts of Stoddard Solvent are Class 3 wastes. Normalized partial Stoddard Solvent analysis results are given in Table 10 (per Anne Roberts, USAFOEHL/SA, Brooks AFB).

**Table 10**
**TYPICAL COMPOSITION OF STODDARD SOLVENT**

| Pollutant or Property | Concentration (Volume %) |
|---|---|
| C-7 | 0.04 |
| Toluene | 0.11 |
| C-8 | 0.30 |
| Xylene, meta- and para- | 1.04 |
| Xylene, ortho- | 0.30 |
| C-9 | 30.35 |
| C-10 | 41.82 |
| C-11 | 24.43 |
| C-12 | 1.60 |
| C-13 | 0.01 |

(2) PD-680.

PD-680 is primarily composed of 9- to 14-carbon atom normal alkanes, with the 10- and 11-carbon atom alkanes comprising most of the hydrocarbon mixture. Wastewater containing dilute PD-680 is a Class 1 waste. Table 11 contains normalized partial analysis results for PD-680 and PD-680 type II (per Anne Roberts, USAFOEHL/SA, Brooks AFB).

## Table 11
## TYPICAL COMPOSITION OF PD-680

| Pollutant or | Concentration (Volume %) | |
| Property | PD-680 | PD-680 Type II |
| --- | --- | --- |
| C-9 | 0.02 | 0.19 |
| C-10 | 5.30 | 13.52 |
| C-11 | 80.41 | 60.96 |
| C-12 | 13.99 | 23.63 |
| C-13 | 0.28 | 1.67 |
| C-14 | 0.00 | 0.02 |

(3) JP-4 Jet Fuel.

Jet fuel is found periodically in wastewater generated at various sites. The washdown of small fuel spills or cleaning of aircraft, aircraft engines and engine parts, for example, contribute to jet fuel in wastewater. JP-4 contains significant amounts of 5- to 15-carbon atom normal alkanes and is rich in aromatics. Wastewaters may contain oxidation products of jet fuel at locations where jet fuel is introduced as a contaminant. For example, phthalates, resulting from the partial oxidation of xylene found in jet fuel, may be present in aircraft washrack wastewater (samples from Dover AFB taken in Feb, Mar 1986). Table 12 contains normalized partial analysis results for JP-4 (per Anne Roberts, USAFOEHL/SA, Brooks AFB).

B. Discharge Limits

Title 40 of the Code of Federal Regulations (40 CFR--Protection of Environment) contains pretreatment and hazardous waste standards which are germane to many of the operations discussed in the previous section. The pretreatment standards apply to specific industries and processes. Each pretreatment standard provides discharge limits for contaminants normally associated with a particular process. Hazardous waste regulations, on the other hand, are specific to the contaminants in and characteristics of the wastewater, and apply to wastewater streams not covered by the pretreatment standards.

## Table 12
## TYPICAL COMPOSITION OF JP-4 JET FUEL

| Pollutant or Property | Concentration (Volume %) |
|---|---|
| C-5 | 4.31 |
| C-6 | 13.00 |
| Benzene | 7.07 |
| C-7 | 13.00 |
| Toluene | 11.39 |
| C-8 | 8.63 |
| Xylene, meta- and para- | 6.53 |
| Xylene, ortho- | 1.62 |
| C-9 | 6.23 |
| C-10 | 5.75 |
| C-11 | 7.79 |
| C-12 | 6.11 |
| C-13 | 4.25 |
| C-14 | 2.88 |
| C-15 | 1.08 |
| C-16 | 0.24 |
| C-17 | 0.06 |
| C-18 | 0.04 |
| C-19 | 0.02 |

The federal regulations which are relevant to most wastewater-generating processes on Air Force bases are listed below:

Part 403--General pretreatment regulations for existing and new sources of pollution
Part 413--Electroplating point source category
Part 433--Metal finishing point source category
Part 459--Photographic point source category
Part 261--Identification and Listing of Hazardous Waste

A list of over one hundred "toxic organics" (organic priority pollutants) listed in both 40 CFR Part 413 and Part 433 is reproduced as Table 13.

## Table 13
## TOTAL TOXIC ORGANICS

Acenaphthene
Acrolein
Acrylonitrile
Benzene
Benzidine
Carbon tetrachloride
Chlorobenzene
1,2,4-Trichlorobenzene
Hexachlorobenzene
1,2-Dichloroethane
1,1,1-Trichloroethane
Hexachloroethane
1,1-Dichloroethane
1,1,2-Trichloroethane
1,1,2,2-Tetrachloroethane
Chloroethane
Bis(2-chloroethyl)ether
2-Chloroethyl vinyl ether (mixed)
2-Chloronaphthalene
2,4,6-Trichlorophenol
Parachlorometa cresol
Chloroform
2-Chlorophenol
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3-Dichlorobenzene
1,1-Dichloroethylene
1,2-Trans-dichloroethylene
2,4-Dichlorophenol
1,2-Dichloropropane (1,3-dichloropropene)
2,4-Dimethylphenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
1,2-Diphenylhydrazine
Ethylbenzene
Fluoranthene
4-Chlorophenyl phenyl ether
4-Bromophenyl phenyl ether
Bis(2-chloroisopropyl)ether

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Table 13 (continued)

Bis(2-chloroethoxy)methane
Methylene chloride
Methyl chloride
Bromoform
Dichlorobromomethane
Chlorodibromomethane
Hexachlorobutadiene
Hexachlorocyolopentadiene
Isophorone
Naphthalene
Nitrobenzene
2-Nitrophenol
4-Nitrophenol
2,4-Dinitrophenol
4,6-Dinitro-o-cresol
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine
Pentachlorophenol
Phenol
Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Di-n-octyl phthalate
Diethyl phthalate
Dimethyl phthalate
1,2-Benzanthracene (benzo(a)anthracene)
Benzo(a)pyrene (3,4-benzopyrene)
3,4-Benzofluoranthene (benzo(b)fluoranthene)
11,12-Benzofluoranthene (benzo(k)fluoranthene)
Chrysene
Acenaphthylene
Anthracene
1,12-Benzoperylene (benzo(ghi)perylene)
Fluorene
Phenanthrene
1,2:5,6-Dibenzanthracene (dibenzo(a,h)anthracene)
Indeno(1,2,3-cd)pyrene (2,3-o-phenylene pyrene)
Pyrene
Tetrachloroethylene (perchloroethylene)
Toluene

Table 13 (continued)

Trichloroethylene
Vinyl chloride (chloroethylene)
Aldrin
Dieldrin
Chlordane (technical mixture and metabolites)
4,4-DDT
4,4-DDE (p,p-DDX)
4,4-DDD (p,p-TDE)
Alpha-endosulfan
Beta-endosulfan
Endosulfan sulfate
Endrin
Endrin aldehyde
Heptachlor
Heptachlor epoxide
(BHC--Hexachlorocyclohexane)
  Alpha-BHC
  Beta-BHC
  Gamma-BHC
  Delta-BHC
(PCB--Polychlorinated biphenyls)
  PCB-1242 (Arochlor 1242)
  PCB-1254 (Arochlor 1254)
  PCB-1221 (Arochlor 1221)
  PCB-1232 (Arochlor 1232)
  PCB-1248 (Arochlor 1248)
  PCB-1260 (Arochlor 1260)
  PCB-1016 (Arochlor 1016)
Toxaphene
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)

These "toxic organics" are lumped together to comprise a single contaminant, total toxic organics (TTO), for which discharge limits are provided.

The standards and explanations which follow are taken from relevant parts of 40 CFR.

1. Part 403

General guidelines to help determine which materials can and cannot be discharged into a POTW are provided in Part 403. Because the wastewater is assumed to be discharged into a

POTW, some of the regulations in this part are closely tied to the National Pollution Discharge Elimination System (NPDES) permit of the POTW receiving the wastewater. Highlights from Part 403 are given below:

a. State or local law covering the same pollutants and discharges governed by the pretreatment standards applies when the requirements set forth in the state or local law are more stringent than those provided in the pretreatment standards.

b. Pollutants discharged into a POTW by a nondomestic source must not pass through or interfere with the operation or performance of the POTW. In this context, "pass through" means that the pollutants in the discharge exit the POTW in quantities that cause the POTW to incur a violation of its discharge permit. "Interfere" means that the discharge disrupts treatment processes at the POTW to an extent that the POTW incurs a violation of its discharge permit.

c. Pollutants which create a fire or explosion hazard in the POTW are prohibited.

d. Pollutants which cause corrosive structural damage to the POTW are prohibited. Discharges to the POTW must not have a pH lower than 5.0 unless the POTW is specifically designed to accommodate such discharges.

e. Solid or viscous pollutants in amounts which will cause flow obstruction in the POTW are prohibited.

f. Discharges which are hot enough to inhibit biological activity in the POTW are prohibited. Discharges must not cause the temperature at the POTW to exceed 40°C unless the NPDES Director or Regional Administrator approves alternate temperature limits at the request of the POTW.

g. A POTW can develop or, in many cases, is required to develop limits in conjunction with pretreatment programs, as outlined in section 403.8 of 40 CFR. However, the limits cannot be enforced without the POTW giving individual notice to persons or groups who have requested such notice and an opportunity to respond.

h. Pollutant discharge limits may be expressed in concentration or mass units.

i. Dilution as a substitution for treatment is prohibited. However, the combining of two or more wastewater streams is allowed if the combined flow is to be treated. Alternative limits for the treated, combined wastewater discharge may be derived by the POTW or by the Industrial User (i.e., the Air Force), subject to written concurrence of the POTW. Formulae for the calculation of alternative mass and concentration limits are given in section 403.6 of 40 CFR, but alternative limits may not be used if the calculation results in levels below the analytical detection limit for any of the regulated pollutants. Self monitoring to insure compliance with the alternative limit is required.

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## 2. Part 413

The various types of electroplating operations covered in Part 413 are listed below:

Electroplating of common metals
Electroplating of precious metals
Electroplating of specialty metals
Anodizing
Coating
Chemical Etching and Milling
Electroless Plating
Printed circuit board

Limits for different metals and metal combinations are specified for the different types of electroplating. However, the limits for individual metals and other wastewater characteristics do not vary. Instead, they are a function of the wastewater discharge rate. Table 14 includes all metals and properties covered in Part 413.

### Table 14
### ELECTROPLATING WASTEWATER PRETREATMENT EFFLUENT LIMITS

| Discharge Rate: | Less than 38,000 l/day | | 38,000 l/day or more | |
|---|---|---|---|---|
| Pollutant or Property | Maximum 1-day Average(mg/l) | Maximum Average of 4 Consecutive Daily Averages (mg/l) | Maximum 1-day Average(mg/l) | Maximum Average of 4 Consecutive Daily Averages (mg/l) |
| Cyanide, A* | 5.0 | 2.7 | -- | -- |
| Cyanide, T* | -- | -- | 1.9 | 1.0 |
| Cadmium | 1.2 | 0.7 | 1.2 | 0.7 |
| Copper | -- | -- | 4.5 | 2.7 |
| Chromium | -- | -- | 7.0 | 4.0 |
| Lead | 0.6 | 0.4 | 0.6 | 0.4 |
| Nickel | -- | -- | 4.1 | 2.6 |
| Silver | -- | -- | 1.2 | 0.7 |
| Zinc | -- | -- | 4.2 | 2.6 |
| Total Metals# | -- | -- | 10.5 | 6.8 |
| TSS | -- | -- | 20.0 | 13.4 |
| TTO## | 4.57 | -- | 2.13 | -- |
| pH | | -- | 7.5-10.0** | 7.5-10.0** |

*"Cyanide, A" means cyanide amenable to chlorination, while "Cyanide, T" means total cyanide
#Total metals is defined as the sum of copper, nickel, chromium and zinc mass concentrations.
**pH units rather than mg/l
##TTO = Total Toxic Organics, refer to Table 13

## 3. Part 433

Operations listed in 4O CFR to which the pretreatment standards in Part 433 apply include:

Electroplating
Coating (chromating--i.e., Alodining)
Cleaning
Solvent Degreasing
Paint Stripping
Painting

Pretreatment facility effluent limits on concentrations for metal finishing are given in Table 15. Values listed for metals and cyanide reflect total concentrations for all forms of those pollutants. Limits for different processes include different pollutants and parameters. Table 15 lists all pollutants and parameters included in Part 433.

## Table 15
## METAL FINISHING WASTEWATER PRETREATMENT EFFLUENT LIMITS

| Pollutant or Property | Maximum 1-day Concentration (mg/l) | Maximum Monthly-Average Concentration (mg/l) |
|---|---|---|
| Cadmium | 0.69 | 0.26 |
| Chromium | 2.77 | 1.71 |
| Copper | 3.38 | 2.07 |
| Lead | 0.69 | 0.43 |
| Nickel | 3.98 | 2.38 |
| Silver | 0.43 | 0.24 |
| Zinc | 2.61 | 1.48 |
| Cyanide | 1.20 | 0.65 |
| TTO | 2.13 | -- |
| Oil and Grease | 52 | 26 |
| Total Suspended Solids | 60 | 31 |
| pH | 6.0-9.0* | 6.0-9.0* |

*pH units rather than mg/l

## 4. Part 459

Pretreatment facility effluent limits for photographic processing are given in Table 16. The numbers in Table 16 for the pH values are in pH units while the numbers for silver and cyanide are in the unusual units of kg/1000 m$^2$ of articles processed or printed (e.g., paper prints, slides, negatives, movie film). Figures in parentheses are in lbs/1000 ft$^2$.

## Table 16
## PHOTOGRAPHIC PROCESSING WASTEWATER PRETREATMENT
## EFFLUENT LIMITS

| Pollutant or Property | Maximum 1-day Concentration | Maximum Monthly-Average Concentration |
| --- | --- | --- |
| Silver | 0.14 (0.030) | 0.07 (0.015) |
| Cyanide | 0.18 (0.038) | 0.09 (0.019) |
| pH | 6.0-9.0 | 6.0-9.0 |

5. Part 261

Part 261 defines hazardous waste and other terms needed to determine the proper disposal method for waste streams. Wastewater streams generated on Air Force bases most likely to be regulated as hazardous wastes are solid wastes exhibiting the characteristic of EP toxicity. (A solid waste as defined in 40 CFR is not necessarily a solid.) Hazardous wastes are subject to regulation under several parts of 40 CFR, and cannot be discharged into a sanitary sewer system unless they have been excluded from regulation under a particular provision in Part 261. For example, a waste that would otherwise be considered a hazardous waste is excluded for conditionally exempt small quantity generators. This waste is conditionally excluded if no more than 100 kg of hazardous waste are generated per month and the waste meets specific requirements described in section 261.5. The parts of 40 CFR regulating hazardous wastes are:

Part 262--Standards applicable to generators of hazardous waste

Part 263--Standards applicable to transporters of hazardous waste

Part 264--Standards for owners and operators of hazardous waste treatment, storage, and disposal facilities

Part 265--Interim status standards for owners and operators of hazardous waste treatment, storage, and disposal facilities

Part 266--Standards for the management of specific hazardous wastes and specific types of hazardous waste management facilities

Part 270--EPA administered permit programs: The Hazardous Waste Permit Program

The following definitions (taken from Part 261) are provided to give a better understanding of what is and what is not regulated as a hazardous waste under 40 CFR.

A solid waste is defined as any material that is (1) abandoned (i.e., disposed of; burned or incinerated; or treated before or in lieu of being abandoned by being disposed of, burned or incinerated), (2) recycled, or (3) not excluded by section 261.4(a) or excluded by variance granted under sections 260.30 and 260.31. Sections 260.30 and 260.31 specify materials, processes, and process streams which are defined to be hazardous wastes. Section 261.4(a) excludes the following wastes from being solid wastes:

a. Domestic sewage

b. Any mixture of domestic sewage and other wastes that passes through a sewer system to a publicly-owned treatment works for treatment

c. Industrial wastewater discharges that are point source discharges subject to regulation under section 402 of the Clean Water Act

d. Irrigation return flows

e. Source, special nuclear or by-product material

f. Materials subjected to in-situ mining techniques which are not removed from the ground as part of the extraction process

g. Pulping liquors that are reclaimed in a pulping liquor recovery furnace and then reused in the pulping process, unless it is accumulated speculatively

h. Spent sulfuric acid used to produce virgin sulfuric acid, unless it is accumulated speculatively

i. Spent sulfuric acid used to produce virgin sulfuric acid, unless it is accumulated speculatively.

A hazardous waste is defined as a solid waste which is: (1) not specifically excluded under section 261.4(b) (e.g., household waste, waste generated from the growing and harvesting of agricultural crops, animal manures), (2) listed in Part 261, Subpart D and not excluded by petition (sections 260.20 and 260.22); (3) exhibits characteristics of ignitability, corrosivity, reactivity, or EP toxicity; or (4) is a mixture of a solid waste and a waste which is hazardous solely due to the characteristics listed in (3) above unless it no longer exhibits those characteristics. (See section 261.3 of 4O CFR for details.)

Various on-base operations (e.g., acid neutralization in the battery shop, pesticide dilution in the entimology shop) can generate small amounts of wastewater which exhibit the characteristic of EP toxicity based on concentrations of specific contaminants in the wastewater. Table 17 lists maximum concentrations for the characteristic of EP toxicity for various materials.

Wastewater from processes not covered by the pretreatment standards (400 portion of 40 CFR) which contain specific materials in concentrations greater than those listed in Table 17 must be disposed of as hazardous wastes and cannot be discharged to the sanitary sewer. However, as implied above, some hazardous wastes can be diluted, unlike wastewaters covered by the pretreatment standards as specified in section 403.6. Once a hazardous waste which is hazardous solely due to ignitability, reactivity, corrosivity, or EP toxicity is diluted so that it no longer possesses those characteristics, it is no longer a hazardous waste and can be discharged to the sanitary sewer. But until it is diluted, all the hazardous waste regulations concerning transport,

record keeping, etc., apply. This means, for example, that the battery shop must keep records of lead concentrations in neutralized battery acid, and dilute the neutralized acid if necessary to assure that no wastewater containing a lead concentration greater than 5.0 mg/l is discharged to the sanitary sewer. Thus, the discharge of neutralized acid should be governed by both solution pH and lead concentration.

### Table 17
### MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY

| Pollutant | Maximum concentration (mg/l) |
|---|---|
| Arsenic | 5.0 |
| Barium | 100.0 |
| Cadmium | 1.0 |
| Chromium | 5.0 |
| Lead | 5.0 |
| Mercury | 0.2 |
| Selenium | 1.0 |
| Silver | 5.0 |
| Endrin | 0.02 |
| Lindane | 0.4 |
| Methoxychlor | 10.0 |
| Toxaphene | 0.5 |
| 2,4-D | 10.0 |
| 2,4,5-TP Silvex | 1.0 |

6. Inhibitory Pollutants

Release of wastes that inhibit downstream treatment processes is prohibited. This implies discharge concentration limits on other materials. In addition to the contaminant discharge limits for streams specified in 40 CFR, Table 18 lists pollutant threshold concentrations which inhibit biological treatment processes and, therefore, should not be exceeded. Unless otherwise indicated. concentrations are given in mg/l.

## Table 18
## THRESHOLD CONCENTRATIONS OF POLLUTANTS INHIBITORY TO BIOLOGICAL TREATMENT PROCESSES

| Pollutant | Process | | |
| --- | --- | --- | --- |
| | Aerobic | Anaerobic | Nitrification |
| **INORGANIC** | | | |
| Aluminum | $15\text{-}26^A$ | | |
| Ammonia | $480^A$ | $1500^{A,B,C}$ | |
| Arsenic | $0.1^A$ | $1.6^A$ | |
| Borate (Boron) | $0.05\text{-}100^A$ $1.0^{B,C}$ | $2^A$ | |
| Cadmium | $10\text{-}100^A$ | $0.02^{A,B,C}$ | |
| Calcium | $2500^A$ | $2500^{B,C}$ | |
| Chromium | | | |
| $(Cr^{+6})$ | $1\text{-}10^A$ $2.0^{B,C}$ | $5\text{-}50^A$ $5.0^{B,C}$ | $0.25^A$ $2.0^{B,C}$ |
| $(Cr^{+3})$ | $50^A$ $2.0^{B,C}$ | $50\text{-}500^A$ $2000^{B,C}$ | |
| Copper | $1.0^{A,B,C}$ | $1.0\text{-}10^A$ $1.0^{B,C}$ | $0.005\text{-}0.5^A$ $0.5^{B,C}$ |
| Cyanide (HCN) | $0.1\text{-}5^A$ | $4^A$ $1.0^{B,C}$ | $0.34^A$ $2.0^{B,C}$ |
| Iron | $1000^A$ | $5^A$ | |
| Lead | $0.1^{A,B,C}$ | | $0.5^{A,B}$ |
| Magnesium | | $1000^{A,B,C}$ | $50^A$ |
| Manganese | $10^A$ | | |
| Mercury | $0.1\text{-}5.0^A$ | $1365^A$ | |
| Nickel | $1.0\text{-}2.5^A$ $1.0^{B,C}$ | $2.0^{B,C}$ | $0.25^A$ $0.5^{B,C}$ |
| Potassium | | $2500^{B,C}$ | |
| Seawater | | | $50(\%)^D$ |
| Silver | $5^A$ $0.03^{B,C}$ | | |
| Sodium | | $3500^{A,B,C}$ | - |
| Sulfate | | $500^{B,C}$ | $500^A$ |
| Sulfide | | $50^A$ $100^{B,C}$ | |
| Vanadium | $10^{B,C}$ | | |

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Table 18 (continued)

| Pollutant | Process | | |
| --- | --- | --- | --- |
| | Aerobic | Anaerobic | Nitrification |
| Zinc | $0.08\text{-}10^A$ | $2\text{-}50^A$ | $0.08\text{-}0.5^A$ |
| | $5.0^{B,C}$ | $5.0^{B,C}$ | $5.0^{B,C}$ |

### ALCOHOLS

| Pollutant | Aerobic | Anaerobic | Nitrification |
| --- | --- | --- | --- |
| Allyl | | $100^A$ | |
| Crotonyl | | $500^A$ | |
| Heptyl | | $500^A$ | |
| Hexyl | | $1000^A$ | |
| Octyl | | $200^A$ | |
| Propargyl | | $500^A$ | |

### PHENOLS

| Pollutant | Aerobic | Anaerobic | Nitrification |
| --- | --- | --- | --- |
| Phenol | $200^A$ | | $4\text{-}10^A$ |
| Cresol | | | $4\text{-}16^A$ |
| 2-4 Dinitrophenol | | | $150^A$ |

### HALOGENATED ORGANICS

| Pollutant | Aerobic | Anaerobic | Nitrification |
| --- | --- | --- | --- |
| Allyl Chloride | | | $180^A$ |
| Carbon tetrachloride | | $10\text{-}20^A$ | |
| Chloroform (tri-chloromethane) | $18.0^{B,C}$ | $10\text{-}16^A$ $0.10^{B,C}$ | |
| Dichlorophenol | | $1^A$ | $50^A$ |
| 1-2 Dichloroethane | | $1^A$ | |
| Hexachlorocyclohexane | | $48^A$ | |
| Methylene Chloride | | $1\text{-}3^A$ $1.0^{B,C}$ | |
| Pentachlorophenol | | $0.4^{A,B,C}$ | |
| Perchloroethylene (tetra-chloroethylene) | | $20^A$ | |
| 1,1,1-Trichloroethane | | $1^{A,B,C}$ | |
| Trichloroethylene | | $20^A$ | |
| Trichlorofluoroethane | | $0.7^{A,B,C}$ | |
| Trichlorotrifluoroethane | | $5.0^{A,B,C}$ | |

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Table 18 (continued)

| Pollutant | Aerobic | Anaerobic | Nitrification |
|---|---|---|---|
| | | Process | |
| **MISC. ORGANICS** | | | |
| Acrylonitrile | | $5.0^{A,B,C}$ | |
| Analine | | | $0.65^A$ |
| *Benzene* | | $50^{B,C}$ | |
| EDTA | | | $300^A$ |
| Pyridine | | | $100^A$ |
| Total oil (petroleum origin) | $50^{B,C}$ | $50^{B,C}$ | $50^{B,C}$ |

[A]U.S.EPA, 1977, [B]Eckenfelder,1980, [C]Cameron and Cross, 1976, [D]Kawasaki, 1986.

Materials not listed in Table 18 which are suspected of having inhibitory effects on downstream biological processes should be tested. Procedures for determining inhibitory threshold concentrations are described by Hovious et al. (1973) for anaerobic processes and by Lewandowski (1987) for biological reactors, in general.

## C. Treatment Process Alternatives

Wastewater contaminant concentrations can be reduced by dilution, physical separation, volatilization, sorption, extraction or bioaccumulation, biotransformation, chemical reaction, or some combination of these processes. Dilution is prohibited as a substitute for treatment for processes subject to the pretreatment standards (400 portion of 40 CFR), but it is allowed for hazardous wastes that are classified as hazardous solely because they exhibit the characteristics of ignitability, corrosivity, reactivity, or EP toxicity. Dilution of such a hazardous waste to the extent that it no longer exhibits those characteristics usually transforms it into a waste that can be discarded readily (e.g., discharging it into the sanitary sewer). However, until it is diluted, the waste is a hazardous waste and is subject to regulations concerning record keeping, storage, transport, etc., for hazardous wastes.

Processes falling into the other treatment categories listed above are discussed in the rest of this report. Design procedures and sample calculations are provided in the Appendixes.

Immiscible liquids (e.g., oils) and suspended solids containing concentrated pollutant forms can be removed from wastewater by gravity settling, coalescence, filtration, or some physical means, reducing the complexity and extent of treatment required for the wastewater. However, most contaminants are dissolved in wastewater because their concentrations are below solubility limits.

Only processes which change the chemical structure and properties of a contaminant (i.e., biotransformation and chemical reaction) provide a solution to the pollution problem. Other processes affect contaminant distribution. For example, air stripping of volatile organic contaminants converts a water pollution problem into an air pollution problem, and activated carbon adsorption of a dissolved metal converts a water pollution problem into a solid disposal problem.

Removal efficiency ranges and average achievable effluent concentrations for various processes and specific pollutants are reported in the EPA Treatability Manual, Vol. I (USEPA,1980a). Table 20 lists some of these published values (in percent and micrograms/liter, respectively) for pollutants and processes of interest. Range entries having only one number indicate that only one data point is available. To facilitate the presentation of data, pollutants were number-coded, and processes were letter-coded. A listing of the codes are presented in Table 19.

### Table 19
### POLLUTANT AND PRETREATMENT PROCESS CODES

Pollutants

METALS AND INORGANICS

| | | | |
|---|---|---|---|
| 1 | Cadmium | 5 | Lead |
| 2 | Chromium | 6 | Mercury |
| 3 | Copper | 7 | Silver |
| 4 | Cyanide (total) | 8 | Zinc |

PHENOLS

| | | | |
|---|---|---|---|
| 9 | Phenol | 10 | Pentachlorophenol |

AROMATICS

| | | | |
|---|---|---|---|
| 11 | Benzene | 13 | Toluene |
| 12 | Ethylbenzene | 14 | Xylene |

HALOGENATED HYDROCARBONS

| | | | |
|---|---|---|---|
| 15 | Methyl Chloride | 20 | 1,2-Dichloroethane |
| 16 | Methylene Chloride | 21 | 1,1,1-Trichloroethane |
| 17 | Chloroform | 22 | Trichloroethylene |
| 18 | Carbon tetrachloride | 23 | 1,1-Dichloroethylene |
| 19 | Chloroethane | 24 | Tetrachloroethylene |

Pretreatment Processes

A  Gas flotation
B  Gas flotation with chemical addition (calcium chloride, polymer)
C  Gas flotation with chemical addition (alum, polymer)

Table 19 (continued)

D  Filtration
E  Sedimentation
F  Sedimentation with chemical addition (alum, lime)
G  Sedimentation with chemical addition (ferric sulfate, lime)
H  Sedimentation with chemical addition (lime, polymer)
I  Sedimentation with chemical addition (sulfide)
J  Aerated lagoons
K  Trickling filters
L  Ultrafiltration
M  Ozonation
N  Chlorination
O  Ion exchange
P  Activated sludge
Q  Activated sludge with powdered activated carbon
R  Granular activated carbon adsorption
S  Reverse osmosis

## Table 20
### PRETREATMENT PROCESS REMOVAL EFFICIENCY RANGES
### AVERAGE ACHIEVABLE EFFLUENT CONCENTRATIONS

| Pollutant | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Process | | | | | | |
| A | - | 40-58/300 | 69/5 | - | 49-82/110 | - |
| B | 79-98/17 | 51-67/330 | 78-91/300 | 2-5/290 | 97-98/150 | 68-90/0.8 |
| C | - | 19/360 | 19/660 | 61/10 | - | 33/1 |
| D | 39-99/20 | 95/610* | 40-99/200 | 10-99/50 | 36-99/140 | 45-86/340 |
| E | 72-99/210 | 79-99/1200 | 66-99/73 | 31-90/330 | 69-99/420 | 50-99/6.1 |
| F | - | 72/31 | 62-88/36 | 70-80/17 | 50/200 | 71/20 |
| G | 25-50/6 | 55-95/3.3 | 72-92/21 | - | 40-96/3 | 30-60/0.2 |
| H | 27-93/16 | 86-98/120# | 87-99/56 | 69-89/21 | 72-98/210 | - |
| I | 50-99/9 | 97-99/40 | 98-99/260 | - | 93-96/100 | 99/20 |
| J | >97/<2 | 63-99/380 | 49-94/40 | 45-91/100 | 86-93/50 | 99/0.1 |
| K | - | - | - | 79/16 | - | - |
| L | 83-93/8 | 67/2900 | 73-90/700 | - | 74-95/1000 | 15-20/0.6 |
| M | - | - | - | 81-99/2100 | 29/22 | - |
| N | - | - | 14/320 | 84-99/38 | - | - |
| O | >99/10 | 99/10 | 98-99/95 | 98-99/65 | 99/10 | - |
| P | 31-99/4 | 45-99/910 | 52-99/43 | 18-90/520 | 49-99/40 | 30-87/0.8 |

Table 20 (continued)

| Pollutant | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Q | - | 87-97/55@ | 52-96/17 | 62-69/28 | 39-78/28 | - |
| R | 34-99/12 | 34-95/60$ | 47-85/66 | 57-90/20 | 14-72/46 | 33-99/1.6 |
| S | 13-50/13 | >99/15* | 73-99/1600 | 43-97/2200 | 31-99/210 | 22-60/0.5 |

* $Cr^{+3}$ only; # 41-82/8.5 for $Cr^{+6}$ only;

@ 41-64/20 for $Cr^{+6}$ only; $ >33/<20 for $Cr^{+6}$ only

ND Not Detected

| Pollutant | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|
| Process | | | | | | |
| A | - | 11-22/27000 | 26-51/1200 | - | - | >99/ND |
| B | 24-48/13 | - | 46-80/87 | 0/- | 0/- | 40-99/280 |
| C | 46/66 | 10/2300 | 0/- | - | - | 0/- |
| D | 11-50/22 | 39-99/940 | 26-93/3400 | 29-87/7.5 | 28-99/45 | 75-99/2.1 |
| E | 78-99/45 | 71-99/2600 | 40-99/21 | 55/24 | 23-63/85 | 47-78/1000 |
| F | - | 55-99/3400 | 48-96/25 | - | 50/46 | 97-98/11 |
| G | 79-97/12 | 79-97/12 | - | - | - | - |
| H | 0/- | 84-99/410 | 18-37/10 | - | 0/- | - |
| I | 90-99/25 | 98-99/140 | - | - | - | - |
| J | - | 55-99/180 | 55-99/14 | 71/10 | 56-95/16 | 78-94/10 |
| K | - | - | 0/- | 0/- | - | - |
| L | - | 78-98/8600 | - | - | - | - |
| M | 0/- | 32-96/260 | - | - | - | - |
| N | - | - | - | - | - | - |
| O | >99/<10 | 97/400 | - | - | - | - |
| P | 31-96/32 | 35-92/200 | 82-99/79 | 70-99/240 | 49-99/4100 | 80-99/170 |
| Q | - | 58-98/110 | - | - | - | - |
| R | 7-36/25 | 40-99/440 | 60-96/0.7 | 63-97/13 | 48-80/73 | 0/- |
| S | 31-92/25 | 83-99/530 | 33-80/2.9 | - | 43-80/1.5 | - |

ND Not Detected

| Pollutant | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|
| Process | | | | | | |
| A | 92/ND | - | - | | 0/- | |
| B | 19-65/1000 | - | - | 2-7/2200 | 31-74/6 | 50/1 |
| C | 10/4.5 | - | - | 84/8 | 0/- | 76/410 |

Table 20 (continued)

| Pollutant | 13 | 14 | 15 | 16 | 17 | 18 |
|-----------|-----|-----|-----|-----|-----|-----|
| D | - | - | 87/0.4 | 14-62/2400 | 0/- | 73-93/32 |
| E | - | - | 59-99/64 | 38-88/530 | 16-81/110 | - |
| F | - | - | - | 13/2000 | 0/- | 17/10 |
| G | - | - | - | - | - | - |
| H | - | - | - | 0/- | 26-78/9 | - |
| I | - | - | - | - | - | - |
| J | 72-95/14 | - | 91/5 | 65-97/390 | 36-57/340 | - |
| K | - | 0/- | - | 0/- | 0/- | - |
| L | - | - | - | - | - | - |
| M | 15-31/1 | - | - | 0/- | - | - |
| N | - | - | - | - | - | - |
| O | - | - | - | - | - | - |
| P | 49-99/57 | 0/- | - | 21-99/95 | 63-99/13 | 0/- |
| Q | - | - | - | - | - | - |
| R | 38-99/80 | - | - | 31-92/140 | 67-99/11 | - |
| S | 4-12/17.5 | - | 0/- | 21-64/5 | 20-79/16 | - |

ND Not Detected

| Pollutant | 19 | 20 | 21 | 22 | 23 | 24 |
|-----------|-----|-----|-----|-----|-----|-----|
| **Process** | | | | | | |
| A | - | - | - | - | - | - |
| B | - | - | 22/14 | 43-86/18 | - | 23-94/580 |
| C | - | - | 74/860 | - | - | 10/0.9 |
| D | - | 0/- | 67-94/710 | 43-90/31 | 52/2 | 30-99/49 |
| E | - | 70/10 | 30-57/19 | 35-71/34 | 0/- | 34-76/23 |
| F | - | - | - | - | - | 95/13 |
| G | - | - | - | - | - | - |
| H | - | - | 0/- | - | - | 0/- |
| I | - | - | - | - | - | - |
| J | - | - | 96/22 | - | - | 60/10 |
| K | - | - | - | 0/- | - | - |
| L | - | - | - | - | - | - |
| M | - | - | - | 0/- | - | - |
| N | - | - | - | - | - | - |
| O | - | - | - | - | - | - |
| P | - | 63/1850 | 74-99/2.4 | 63-99/9 | - | 78-99/2300 |
| Q | - | - | - | - | - | - |
| R | 58-99/71000 | 86-99/230000 | 99/10 | 29-58/2.8 | - | 68/32 |
| S | - | - | - | 60/0.4 | - | - |

ND Not Detected

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It should be recognized that the conditions of the experiments or operations from which data were obtained for the EPA Treatability Manual Vol. I (USEPA, 1980a) and, therefore, for Table 20, are not given. The application of a particular treatment processs to wastewater streams and operating conditions different from those used in the EPA Treatability Manual, Vol. I (USEPA, 1980a) may result in effluent pollutant concentrations outside the reported ranges.

The selection of a pretreatment process or a series of pretreatment processes depends upon many factors, including:

1. the maximum allowable pollutant effluent concentration
2. the potential for generating undesirable by-products
3. the presence of interfering materials
4. the availability of land and capital
5. the availability of manpower and technical support
6. the type of POTW receiving wastewater.

In addition, training of operating personnel to the appropriate level of expertise is essential for reliable performance of any piece of equipment. The selection of a treatment process should be made only after considering the probable characteristics of the treated wastewater. For example, the oxidation of many trace organics could be accomplished by chlorinating the wastewater. However, chlorinated organics resulting from the treatment may present more of a problem than the organics originally present (e.g., chlorinated phenols).

Options for the separation or combination of discrete wastewater streams must also be considered. For example, the separation of two wastewater streams prior to treatment may make the removal of one component relatively easy, compared with its removal from the combined streams. Most of the pretreatment alternatives listed in Table 19 are typically continuous processes. This is especially true of biological processes. In most cases the pH of the feed must be in a narrow range. For these reasons, equalization and neutralization are often performed prior to treatment of the wastewater for the removal of contaminants. With equalization, a holding pond receives wastewater from a single or multiple batch process in order to reduce variability in the quality and flow rate of the wastewater to be treated. Given the volumes and frequency of wastewater discharge into the equalization basin, minimum equalization basin volumes can be readily determined by following the procedures outlined in standard texts and references (e.g., Tchobangolous, 1979; Tsugita, 1981).

Wastewater can be treated by many different processes or process sequences to remove deleterious pollutants and properties. The process sequences given in the following sections are only suggested treatment unit operation sequences. They are not unique, and are recommended on the basis of published literature, published experimental and operating data, and experience.

1. Class 1 Wastewaters

The process sequences suggested in this section are for industrial wastewaters having the following characteristics: high concentration of "nontoxic" organics. The preferred treatment sequence depends on the pH of the solution, presence of surfactants, required removal, and availability of existing treatment facilities. If, for example, the water is from a washrack and

contains high concentrations of alkaline detergents and possibly some PD-680, the emulsified organics will be difficult to remove by physical means without lowering the solution pH (see discussion on ZPC in the section on sedimentation/coagulation). The easiest solution would be to send the wastewater to an existing biological waste treatment facility which already has sufficient buffering capacity in the feed to permit the addition of the alkaline wastewater without greatly affecting the pH of the combined wastewater feed.

If the wastewater is to be treated by itself, several treatment options are available: biological, physical/chemical, and a combination of biological and physical/chemical. The sludge produced in the biological treatment of this waste should be relatively innocuous if no heavy metals are present.

The biological option would require neutralization of the wastewater prior to treatment and may require filtration as a final step, depending on the settling characteristics of the sludge generated in the treatment process. The recommended sequence is:

       a. equalization,
       b. neutralization,
       c. activated sludge,
       d. filtration (if necessary).

The combination treatment scheme (biological and physical/chemical) would reduce the oxidation load on the biological unit, resulting in a smaller biological unit and less sludge production. Filtration is less likely to be necessary as a final step in the following sequence:

       a. equalization,
       b. neutralization,
       c. coalescence,
       d. activated sludge,
       e. filtration (if necessary).

The physical/chemical treatment described below would produce oily sludge which may present disposal problems:

       a. equalization,
       b. neutralization,
       c. alum coagulation.

2. Class 2 Wastewaters

The treatment sequences suggested in this section are for industrial wastewaters having the following characteristics: high organics, low heavy metals. Sludge disposal may be a problem, depending on the metal species and concentrations. The suggested sequence is:

a. equalization,
b. neutralization,
c. activated sludge.

Care must be taken to insure that inhibitory concentrations of metals and toxic organics are not reached. If metal concentrations in the effluent are not sufficiently reduced, additional treatment similar to that recommended for Class 4 wastewaters may be required.

## 3. Class 3 Wastewaters

The treatment sequences suggested in this section are for wastewaters having the following characteristics: trace "toxic" organics. The preferred treatment process depends on the nature of the organic compounds in the water. If the organics are highly volatile (Henry's Law constant greater than 0.005 atm m$^3$/mol, or 0.21 in terms of a mass concentration ratio -- see Riojas et al., 1983, for discussion), the suggested sequence is:

a. equalization,
b. air stripping.

If the organics are not very volatile (Henry's Law constant less than 0.005 atm m$^3$/mol, or 0.21 in terms of mass concentration ratio -- see Riojas et al., 1983, for discussion) and are not highly chlorinated, the suggested sequence is:

a. equalization,
b. mixing with a carbon source (e.g., sewage or molasses).
c. activated sludge.

If the organics are not very volatile and are highly chlorinated:

a. equalization,
b. mixing with a carbon-rich wastewater or feed.
c. anaerobic digestion,
d. reaeration,
e. activated sludge,
f. filtration.
h. air stripping (if necessary).

## 4. Class 4 Wastewaters

The treatment sequences suggested in this section are for wastewaters having the following characteristics: some heavy metals, low organics. The preferred treatment sequence depends on the nature of the metals and the quantity and nature of the organics present. Generally, organics will promote a reducing environment, inhibit settling, and foul (sometimes irreversibly) ion exchanging resin and activated carbon. Removal of metals is commonly accomplished by oxidizing

(e.g., iron, magnesium) or reducing (e.g., chromium) the metal to its least soluble oxidation state, and then separating the precipitate from the solution. The following treatment sequence is suggested if recovery of the metal is not required:

    a. equalization,
    b. oxidation (e.g., aeration, chlorination) or reduction
       (e.g., with sulfur dioxide),
    c. pH adjustment (if necessary),
    d. sedimentation or filtration.

If metal recovery is required, ion exchange technology is commonly utilized. The following treatment sequence is suggested if recovery of the metal is required:

    a. equalization,
    b. filtration,
    c. pH adjustment (if necessary),
    d. ion exchange,
    e. pH adjustment (if necessary).

5. Class 5 Wastewaters

The treatment sequences suggested in this section are for wastewaters having the following characteristics: some heavy metals, cyanide, some organics. Because chemical treatment could result in the liberation of hydrogen cyanide gas, removal of the cyanide is the first step in the treatment of this wastewater (see section on chlorination). The treatment sequence selected depends on many factors, including the type of metals present and recovery requirements, and the type and quantity of organics present. If no metal recovery is required and the major problem associated with the organics is the COD associated with them, the following treatment sequence is suggested:

    a. equalization,
    b. metal reduction (reduction followed by pH adjustment and filtration or
       sedimentation, if necessary),
    c. cyanide removal (e.g., chlorination), and metal oxidation (if necessary),
    d. pH adjustment (if necessary),
    e. sedimentation or filtration.

If the water requires additional treatment for the removal of organics (those originally present in the wastewater as well as the chlorinated organics generated in step 2 above), the wastewater may be treated as described in the treatment section for Class 3 wastewaters.

If metal recovery is required, the following treatment sequence is suggested:

    a. equalization,
    b. cyanide removal (e.g., chlorination),
    c. filtration,

      d. pH adjustment (if necessary),

      e. ion exchange,

      f. pH adjustment (if necessary).

Again, if the wastewater requires additional treatment for the removal of organics, it may be treated as described in the treatment section for Class 3 wastewaters.

Treatment options for photographic processing wastewater have been studied by Donovan et al. (1983). No cyanide was reported in the wastewater studies. Typical characteristics of photographic processing wastewater are given in Table 8. Treatment alternatives considered by Donovan et al. included reverse osmosis, activated carbon adsorption, biological treatment, air stripping and chemical precipitation. The process recommended in the study was reverse osmosis. Many other options for treating photographic processing wastewater have been published and can readily be found. Electroplating wastewater treatment options and recommendations are described in some detail by Cushnie (1985). Cushnie includes suggestions for the handling of generated sludges. The "standard" treatment process sequence prescribed by Cushnie is given below:

      a. chromium reduction (if needed),

      b. cyanide oxidation (if needed),

      c. pH adjustment,

      d. clarification with flocculation/coagulation,

      e. gravity thickening of sludge,

      f. sludge dewatering.

## 6. Class 6 Wastewaters

Various pretreatment processes are recommended for wastewater streams from over seventeen different industries in Federal Guidelines: Pretreatment of Pollunts Introduced into Publicly Owned Treatment Works (USEPA, 1973). Of the industries discussed, the metal finishing industry is relevant to Air Force base operations in that it produces wastewater having characteristics similar to Class 6 wastewater: low BOD and COD, high TDS and heavy metals, high cyanide, and trace oils and grease. Pretreatment unit operation options given are divided into three categories based on the type of treatment process used at the POTW which is to receive the wastewater: suspended biological, fixed biological, and independent physical/chemical. The suggested treatment sequence for suspended and fixed biological systems is:

      a. equalization,

      b. neutralization,

      c. cyanide removal,

      d. chromium reduction,

      e. chemical precipitation (for heavy metals),

      f. solids separation (USEPA, 1973).

The suggested treatment sequence for an independent physical/chemical system is:

a.  equalization,
b.  cyanide removal,
c.  chemical precipitation,
d.  neutralization (USEPA, 1973).

The following process descriptions are included as background information to facilitate the interpretation of data already presented and to give insight into the different water treatment operations. Brief process descriptions and performance data for these and other processes can be found in the EPA Treatability Manual, Vol. III (USEPA, 1980c).

## 7. Gas Flotation

Gas flotation can be used to separate suspended solids or emulsified oils from water (Luthy, 1978). Compressed gas is contacted with part or all of the wastewater or a slip-stream of recycled effluent in a pressurized tank, resulting in the dissolution of gas into the liquid phase. Air is typically used as the flotation gas. Thus, the process is also known as dissolved air flotation (DAF). The pressurized liquid stream proceeds through a pressure relief valve. The drop in pressure causes dissolved gases to come out of solution, forming tiny bubbles. The wastewater (or recycled effluent) that was pressurized is then combined with the rest of the wastewater and goes to an atmospheric separation basin (flotation basin) where the gas bubbles adhere to solid surfaces, making the solid particles more buoyant. The solids rise to the water-atmosphere interface where they accumulate and are skimmed off the top. The flotation basin is also equipped with a scraper on the bottom of the basin to remove solids that are too heavy to float to the water-atmosphere interface.

The application of this process is appropriate for separating emulsified oils and light solids from water, and not, for example, for removing grit and sand. Coagulants or polymers are often added to promote the agglomeration of solids which in turn enhances the collection of bubbles on solids and improves solid/liquid separation efficiency. Equations used in the design of gas flotation facilities are included in Appendix A.

## 8. Filtration

Filtration of a liquid stream is a means of physically separating entrained or suspended solids from the liquid. The accumulated solids can then be removed from the filter by backwashing the filter medium. Backwash water is sent to drying beds or other facilities for final disposal of the solids. Because filters are taken out of service during backwashing, filter installations usually include multiple filters in a parallel flow configuration. A filter bed service run ends when either a breakthrough in suspended solids at the bed outlet occurs, or when too high a pressure drop across the bed under constant flow conditions develops, or the flow rate through the filter bed under constant pressure drop conditions falls below an acceptable level.

Typical filter media are sand, gravel, coal, and rock. Single- and multimedia filters are common in industry. Backwash operations produce segregation of filter media: separation of media having different specific gravities, and the gradation of filter grains within each medium with the smaller grains on the top. Each filter medium has different flow characteristics, and the optimum

filter design is obtained when the solids breakthrough at the bed outlet occurs at the same time as the maximum allowable bed pressure drop is reached. The size and uniformity of a filter medium are, therefore, important design considerations, since fine filter grains result in less bed penetration and higher pressure drop. The effective size of a filter medium is defined as the sieve size that passes 10% of the filter grains. The uniformity coefficient is defined as the ratio of the sieve size that passes 60% of the filter grains to the effective size of the filter medium. The effective size of a sand filter is typically between 0.35 and 0.5 mm. Values of uniformity coefficient are typically between 1.3 and 1.7. Higher uniformity in a filter medium can be obtained by backwashing it and physically removing the upper inch or so of medium from the bed. The use of multimedia filters allows lighter, courser filter media to be located in the upper portion of the filter, producing a lower pressure drop in the upper portion of the bed while unloading the solids-removal burden on the more efficient finer grains.

Upflow filtration has the advantage of directing flow in the direction of decreasing grain size for a single filter medium. From the above discussion about grain size distribution, the advantages are evident; however, there are distinct disadvantages as well. For example, small supply pressure fluctuations can disturb the bed, resulting in premature solids breakthrough. Upflow filtration is not as commonly used as is downflow filtration.

The pressure drop (head loss) across a clean filter bed can readily be calculated from filter and liquid properties and flow conditions using the Carman-Kozeny equation. This is equivalent to Daroy's law under laminar flow conditions. However, because the void spaces in the filter decrease with time due to the accumulation of solids in the filter, the pressure drop is also a function of time. Pressure drop is difficult to predict for a filter already in operation.

Several different mechanisms of particle removal are involved in filtration. For example, equations for single collector removal efficiencies due to interception, diffusion, and gravity are found in many standard texts (e.g., Weber, 1972). The removal efficiency due to diffusion (Brownian motion) decreases with increasing particle diameter, while the removal efficiencies due to interception and gravity increase with increasing particle diameter. Consequently, the overall removal efficiency for a single collector goes through a minimum for suspended particles having a diameter near one micron. However, all three mechanisms involve the contact of the suspended particles in the liquid with the filter grains.

Not all contacts between particles and grains result in permanent removal of the solid from solution. Filters are sometimes precoated with a polymer to increase the likelihood that particles that contact filter grains will stick. The polymer is added to the final stage of the backwash water. Filter precoating is usually practiced only when dealing with a material that is particularly difficult to remove from solution, or when an improvement in the performance of existing filtration facilities is required and other options are not immediately available. Care must be exercised to assure that polymer is not overfed and that filters are adequately backwashed, since a drop in filter backwash efficiency, and consequently in filter performance, could occur otherwise.

A small reduction in the dissolved organics concentration as measured by the soluble COD or soluble BOD of the wastewater is sometimes observed after filtration operation. This is largely due to the film (schmutzdecke) that can form on the top surface of the filter, consisting of

both inorganic and biological material, and the biooxidation of degradable dissolved organics as they pass through it. However, in general, design BOD and COD reductions associated with filtration operations should be restricted to reductions in the concentrations of BOD and COD due to removal of suspended solids. Equations used in the design and evaluation of filters are contained in Appendix B.

### 9. Sedimentation/Coagulation

The objective in sedimentation and coagulation is to remove suspended solids and colloidal material that contribute to the color, odor, and turbidity of water. Some dissolved organics and heavy metals removal usually accompanies the solids removal in these processes. The problem of sludge disposal must be assessed when considering sedimentation/coagulation as a treatment process.

In a sedimentation basin, settleable solids are removed by gravity settling. Under laminar flow conditions (Reynolds number < 10), if only viscous and gravitational forces are involved, Stoke's law can be used to calculate the vertical velocity of suspended solids, while their horizontal velocity is determined by the liquid flow rate and the cross-sectional area of flow in the basin. Stoke's law was derived by assuming that falling particles reach their terminal settling velocity, making the viscous drag force acting on them equal to the force of gravity. The design objective is to allow the solids to reach the bottom of the basin before they reach the basin water outlet. Accumulated solids are removed from the bottom of the basin. Whenever possible, calculated settling basin volumes should be verified by settling tests conducted with the wastewater to be treated.

Some suspended solids are stable and do not settle readily due to repulsive electrostatic force between them. The charges on the particles may be due to ionized functional groups on solid surfaces or adsorption of charged polymers onto surfaces. During dissociation, many functional groups release hydrogen ions or other ions, causing interaction between the functional groups and hydrogen or hydroxide ions in solution. Since functional groups on solids are in equilibrium with the liquid surrounding them, solution pH affects the degree of functional group dissociation and, therefore, influences the surface charge on the suspended solids. The Zero Point of Charge (ZPC) is the pH value which results in a net charge of zero on the suspended solids. Thus, in a solution containing one kind of charged, stable, suspended solids, the particles could be destabilized, allowing them to settle, if the pH of the solution were adjusted to the ZPC of the particles. Different types of particles have distinct ZPC values. For example, bacteria, humic acids, and most organic particles have a ZPC between 2 and 5 while magnesium oxide (MgO) has a ZPC of 12.4. At a pH of 7, therefore, most organic particles would have a negative charge, while MgO would have a positive charge.
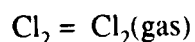
Dissolved ions may accumulate in layers around the particles. The Zeta Potential is defined as the mean potential between the bulk fluid and a suspended particle including its surrounding layers of ions. The Zeta Potential is one of the operating parameters sometimes used in coagulation/sedimentation operations.

In the process of coagulation, suspended solids are destabilized by adding a material (coagulant, also called flocculant) that will form an insoluble, settleable solid (floc) to which suspended solids will be attracted for subsequent settling and removal. The most widely used coagulant is alum (aluminum sulfate). Alum is most effective at pH values near 7. As alum polymerizes, it forms a charged, gelatinous solid which also provides adsorption sites for dissolved organics and heavy metals. Like aluminum ions, ferric ions also form polymer chains: however, floc formed from an iron salt are more stable at elevated pH values (9-10). A rapid-mixing chamber (flash mixer) where the coagulant is added is required to provide vigorous agitation and to assure a uniform coagulant distribution in the bulk fluid. Water leaving the flash mixer goes to a flocculation vessel where gentle stirring promotes the contacting of suspended solids and floc growth. The network of floc is then allowed to settle, trapping more suspended particles as it falls to the bottom of the sedimentation basin (enmeshment). Optimum coagulant dosages are normally determined from jar test results. Because the floc that is formed from inorganic polymers is fragile, organic polymers are sometimes added with the coagulant as floc conditioners. These polymers also promote the removal of organics responsible for color through adsorption. Space-saving clarifiers which provide zones for the three distinct processes (flash mixing, flocculation, and sedimentation) are often used. Design equations for sedimentation basins and clarifiers are included in Appendix C.

## 10. Chlorination

Chlorine has long been used as an oxidizing agent and disinfectant for the treatment of potable water and wastewater. It effectively oxidizes both organic and inorganic pollutants. Chlorine can be applied as a gas, as is typical in industry, or in the form of solid hypochlorite salts of calcium or sodium, as is typical in the treatment of water in small swimming pools. A brief discussion of the water chemistry of chlorine will serve to illuminate potential applications for the chlorination process.

Chlorine gas is soluble in water. Upon hydrolysis, molecular chlorine ($Cl_2$) forms hypochlorous (HOCl) and hydrochloric (HCl) acids. The hydrochloric acid completely dissociates to chlorides ($Cl^-$) and hydrogen ions ($H^+$), while the hypochlorous acid partially dissociates to hypochlorite ions ($OCl^-$) and hydrogen ions. Under equilibrium conditions many chlorine-containing species are present, with the distribution of species being pH dependent. The major equilibrium reactions and constants that apply are presented below. All species shown are in the aqueous phase unless otherwise indicated. The species in brackets ([ ]) represents the numerical value of the molar concentration of that species.

$$Cl_2 = Cl_2(gas) \qquad\qquad K_1 = [Cl_2(gas)]/[Cl_2]$$

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \qquad\qquad K_2 = [HOCl][H^+][Cl^-]/[Cl_2]$$
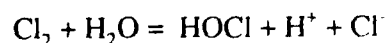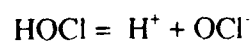
$$HOCl = H^+ + OCl^- \qquad\qquad K_3 = [H^+][OCl^-]/[HOCl]$$

The application of solid hypochlorite salts results in the same equilibrium relationships shown above and the solubility expressions given below.

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$$Ca(OCl)_2 = Ca^{+2} + 2\ OCl^- \qquad\qquad K_{sp,4} = [Ca^{+2}][OCl^-]^2$$

$$NaOCl = Na^+ + OCl^- \qquad\qquad K_{sp,5} = [Na^+][OCl^-]$$
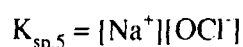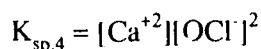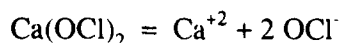
Of the various chlorine species, HOCl has, by far, the greatest germicidal potential. The equilibrium and solubility constants (K's) are a function of temperature. High temperatures and high chloride concentrations favor the formation of molecular chlorine and its consequent loss to the atmosphere as a gas. Low pH, on the other hand, results in higher equilibrium HOCl concentrations.

Reactions of HOCl with organic compounds in water results in trace concentrations of a broad spectrum of products including chloroform and other carcinogens listed as toxic organics in 40 CFR, Part 433. Therefore, wastewater which is heavily laden with organics should not be chlorinated because of the toxic by-products produced.

Reactions of HOCl with compounds such as ammonia, a degradation product of proteins or other nitrogen-containing organics, results in products (e.g., chloramines) which still have oxidizing potential and germicidal qualities, but that are less volatile than and are not directly involved with the formation of molecular chlorine.

Chlorine is widely used in the metal plating industry to react with cyanide. In a series of reactions, chlorine, cyanide and hydroxides are consumed. At low pH values, cyanogen chloride, a volatile and toxic compound, is liberated from aqueous solution. For this reason, the chlorine-cyanide reaction is generally carried out at pH values greater than 10 (Chambers, 1976). The overall reaction is given below:

$$NaCN + 2NaOH + Cl_2 \longrightarrow NaCNO + 2NaCl + H_2O$$
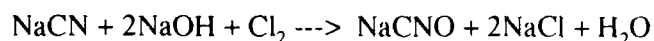
Additional chlorination at pH values between 7.5 and 9 results in the conversion of cyanate to molecular nitrogen and bicarbonate (Chambers, 1976) as shown in the reaction below:

$$2NaCNO + 6NaOH + 3Cl_2 \longrightarrow N_2 + 2NaHCO_3 + 6NaCl + 2H_2O$$
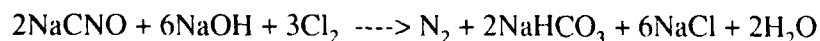
In practice, the total chlorine required for the two reactions is higher than the theoretical 6.82 parts per part cyanide, and the total hydroxide is lower than the theoretical 7.69 parts per part cyanide. This is due to the presence of other materials in the wastewater that react with chlorine, and the presence of alkalinity in the water.

Design equations for oxidation facilities are included in Appendix D.

11. Ozonation

Ozone is the oxidizing agent of choice for potable water supplies if there are no monetary constraints and no residual is needed. It can be used to oxidize both organic and inorganic pollutants. Ozone has almost no effect on pH and produces less toxic by-products than does

chlorination when used as an oxidant in the treatment of organic-laden water. The major products of the complete oxidation of organics by ozone are carbon dioxide, water, and oxygen. However, partial oxidation of some organics produces by-products that are more toxic than the original compounds. Because the ozone molecule is highly reactive and unstable, an ozonated aqueous solution will not maintain a residual ozone concentration for very long. Design considerations and design equations for oxidation facilities are contained in Appendix D.

The most popular method of generating ozone involves the arcing of an electrical current across a gap in an oxygen-containing atmosphere. It is an energy intensive process. To maximize production efficiency, oxygen is used instead of air. The gas containing the ozone is contacted with an aqueous solution to absorb the ozone into the liquid phase. Because ozone is 11.5 times more soluble in water than is oxygen, the ozone is preferentially absorbed while most of the oxygen remains in the gas phase where it can be utilized to generate more ozone.

Ozone can be used as an oxidizing agent to treat wastewaters containing a variety of contaminants (e.g., phenols, sulfides, sulfites, mercaptans, cyanides, amines). However, it is generally more expensive to generate and use than is chlorine, and is usually reserved for the treatment of potable water: color reduction, oxidation of iron, manganese, and organics as well as disinfection.

12. Granular Activated Carbon Adsorption

Activated carbon is used in home and industry to purify water. It is used to purify industrial gas and non-aqueous liquid streams well. Activated carbon is generated by the partial pyrolysis of carbonaceous material such as coal, coconut shells, wood, etc. Activated carbon made from wood is given the special name, activated charcoal. Activated carbon is characterized by its large surface area (on the order of 400 to 1200 square meters/gram), high porosity, and a correspondingly large adsorption capacity for many organic and inorganic molecules.

Granular activated carbon (GAC) beds require periodic regeneration or replacement of the carbon. In general, high temperatures and high flow rates result in lower total bed adsorption capacities. The GAC medium also acts as a filter to remove suspended solids from solution.

The pore structure contains most of the surface area of an activated carbon granule. This makes pore diffusion an important consideration in the design of a GAC absorber, since it may be the limiting resistance to mass transfer between the bulk liquid and the adsorption sites on the activated carbon for larger molecules with lower diffusivities. The amount of surface area available for adsorption depends on the pore size distribution and the size of the adsorbing molecule. Adsorption on the surface may be weak, strong, or irreversible. Adsorbing molecules may form a monolayer on the surface, or they may adsorb in multiple layers.

Two mechanisms of adsorption have been proposed. Physisorption is weak, reversible, single- or multilayer adsorption, largely due to electrostatic forces between the adsorbing molecule and the surface. Chemisorption is a stronger, single-layer adsorption due to chemical

interaction between the adsorbing molecule and specific functional groups on the surface. Irreversible adsorption and loss of adsorption capacity of the GAC is associated with chemisorption, although both types of adsorption are present.

In order to predict the performance of a bed of GAC, an equilibrium curve relating the aqueous pollutant concentration and the absorbed concentration (at a constant temperature), termed equilibrium isotherm, is needed. The isotherms for most materials are similar in shape and fit specific mathematical models. The Langmiur, Freundlich, and BET isotherms are among the most widely used isotherms.

The driving force for the adsorption is the deviation from equilibrium conditions. When a bed of GAC is placed in service, the top portion of the bed reaches equilibrium (become exhausted), while the bottom of the bed remains virtually clean. A zone of partially spent GAC proceeds down the column with time. The shape of the concentration profile in this region is generally that of an inverted "S", and the exact shape and degree of spreading is due to hydrodynamic conditions in the bed which control the resistance to mass transfer from the bulk fluid to the GAC granules, and parameters such as pore diameter and molecular diameter which influence the mass transfer resistance due to pore diffusion. When this zone reaches the bottom of the bed, the bed is said to be completely exhausted and regeneration or replacement of the bed is required.

Equilibrium liquid/adsorbed concentration data over limited ranges for most pollutants are given in the EPA Treatability Manual Vol. I (USEPA, 1980a). Design procedures are discussed in Appendix E.

13. Ion Exchange

Ion exchange processes are more expensive than most other water treatment processes. Ion exchange is used when high water purity is required or when it is necessary to remove dissolved ions which are otherwise difficult to remove from water. Ion exchange media require frequent regeneration, and special materials of construction are needed for piping and vessels because of corrosive regenerant solutions. Although natural exchange materials are sometimes used in water-softening applications (the exchange of sodium for dissolved calcium and magnesium), the more expensive and higher capacity man-made ion exchange resins are usually used because of the lower regeneration frequency and higher regeneration efficiency associated with them.

Most synthetic resins have the appearance of small plastic beads, on the order of one to two millimeters in diameter. These beads are formed by long polymeric chains of polystyrene rolled into spheres and made rigid by cross-links of divinyl benzene. Functional groups that give the resin its particular ion-exchange characteristics are attached to the polystyrene matrix.

Oxidation of the resin should be expected with use, resulting in the loss of ion exchange capacity, loss of rigidity (and consequent increase in pressure drop across the bed), and increase in moisture content. Temporary or permanent organic fouling, particularly of anion exchange resins, can also occur when the resin is exposed to organic-laden waters.

Operating in the acid cycle (resin regenerated with acid solution), weak acid and strong acid cation resins are used to replace some or all other dissolved cations, respectively, with hydrogen ions. The pH of the water passing through a cation resin bed operating in the acid cycle would, therefore, drop. Similarly, when operated in the base cycle (resin regenerated with base solution), weak base and strong base anion resins are used to replace some or all other dissolved anions, respectively, with hydroxide ions). The pH of the water passing through an anion resin bed operating in the base cycle increases. Thus, depending on the application, an adjustment in the pH of the treated water may be necessary. Operation of cation beds in the sodium cycle or anion beds in the chloride cycle (resin regenerated with brine solution) would not generally affect the pH of the water being treated.

The removal of a particular ion from solution is primarily governed by the resin equilibrium isotherm for the ion (constant temperature equilibrium relationship between the dissolved concentration and the concentration on the resin) and the total ion exchange capacity of the resin. The equilibrium isotherm and bed depth determine the minimum liquid concentration that can be achieved, while the ion exchange capacity determines the required bed depth to attain a prescribed regeneration frequency. The travel of a saturation front down the bed is similar to that described in the section on GAC.

The efficiency of an ion exchange bed is greatly reduced by channeling through or around the bed. The short-circuiting of relatively untreated water to the bed outlet is not uncommon since ion exchange resin swells or shrinks, depending on the species bound to it. As the bed swells or shrinks, cracks can form in the bed or the resin can separate from the vessel wall. Premature breakthrough can sometimes be avoided by redistributing the resin in the upper portion of the bed midway through the service run; however, care must be taken to keep the relatively fresh resin on the bottom of the bed from mixing with the resin above it which will be closer to exhaustion. Operation of a bed which has pulled away from the vessel wall will result in a bed having exhausted resin near the wall, a core of relatively fresh resin, and an unacceptably high effluent concentration.

The performance of ion exchange resin in the removal of a specific ion depends on several other factors including:

a. the type, age, and condition of the ion exchange resin
b. the presence of fouling agents
c. the type and concentration of regenerant being used, and regeneration efficiency
d. the presence of other ions and ion selectivity
e. the solution temperature and pH
f. the ionic strength of solution

The first, and one of the most critical design choices is the selection of the ion exchange resin. Resin capacity, ion selectivity, liquid temperature, required regeneration chemicals and their concentrations, feed and effluent pH, and exchanged ion recovery must all be considered in the selection of an ion exchange resin.

Once the resin has been chosen, resin capacity data for the resin and solute to be removed from solution determine the service cycle for a given set of operating conditions. The maximum bed height is usually based on the weight that resin can support without suffering damage during normal operating conditions. A fractional multiple of the maximum bed height is usually chosen as an operating bed height.

Effluent quality better than what can normally be produced in a standard ion exchange unit can be obtained by designing the service flow and the regenerant flow in opposite directions. The resin which is brought into contact with fresh regenerant is regenerated to a greater extent than the resin downstream. Downstream resin is regenerated with a solution containing a lower concentration of the regenerating ion and an increasingly high concentration of the ions to be removed from the resin as the flow proceeds through the bed. Upflow operations, however, are generally more difficult to maintain, requiring closer attention from operators.

The feed to an ion exchange unit can sometimes be conditioned to increase the capacity of a bed or decrease the size of the bed. For example, the hexavalent chromium removal capacity of an anion bed can be greatly increased by reducing the pH of the feed, shifting the chromate/dichromate equilibrium toward dichromate and doubling the number of chromium atoms exchanged per exchange site.

The ion concentration in the feed also influences the expected loading of an ion exchange unit. For example, the resin loading that can be expected in an operation designed to remove hexavalent chromium from a *pigment manufacturing process effluent is substantially higher than that of a similar operation designed to remove hexavalent chromium from cooling water blowdown.* (The recovered chromium is recycled to the process in both operations.) This difference in the resin loadings is largely due to the difference in the concentrations of hexavalent chromium in the feeds to the ion exchange units. The chromium concentration in the pigment manufacturing effluent is as high as 2700 mg/l, and the water is low in organics (Robinson et al., 1974). Cooling water blowdown, on the other hand, is warm, rich in organic surfactants and biological growth, and has hexavalent chromium concentrations on the order of 10 mg/l.

As with filter beds having low uniformity coefficients, adverse flow characteristics are associated with resin beds having too wide a range of resin bead diameters. For this reason, beds having a new charge of resin are sometimes backwashed thoroughly, and the top inch of resin containing small beads and bead fragments is discarded prior to placing the bed in service.

Single-use ion exchange resin operations are sometimes economical for the recovery of precious metals. Regeneration facilities are not required because the resin is burned in an incinerator, leaving behind the recovered metal.

Design procedures for ion exchange beds are included in Appendix F.

14. Aerated Lagoons/Activated Sludge/AS-PAC

Many organic pollutants can be readily degraded by microorganisms. The pollutant serves as the substrate (carbon and energy source) for the production of more microorganisms

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(sludge). Utilization of the substrate results in the formation of oxidized organic compounds or complete mineralization of the substrate to carbon dioxide and water. If the pollutant concentration is not high enough to support microbial growth, the feeding of an additional organic substrate (primary substrate) such as molasses or sewage may be required to promote the degradation of the pollutant (secondary substrate).

Three similar aerobic suspended biological growth reactors are the aerated lagoon, activated sludge, and activated sludge with powdered activated carbon processes. The partial conversion of the organic pollutants to active microorganisms means that the liquid-phase pollution problem is transformed into a solid waste disposal problem. The presence of heavy metals, such as chromium which preferentially partition into the solids, usually requires that special care be taken with the disposal of a solid waste product that might otherwise be a useful by-product used as fertilizer, for example. Air pollution problems can also result when volatile organic pollutants are stripped out of the liquid phase during aeration.

An aerated lagoon is a well-mixed pond in which surface aerators or submerged aerators are used to contact the wastewater fed to the pond with air. The active organism population is determined by the liquid detention time (volume/flow rate), substrate, type of organisms present, and temperature. The pollutant removal rate is proportional to the concentration of the pollutant, the active organism concentration, and the liquid detention time.

An activated sludge (AS) plant is a process in which microorganism recycle is used. By recovering and recycling the microorganisms leaving the aeration basin, lower effluent concentrations and higher pollutant removal efficiencies are possible. In general, the pollutant concentration in the effluent decreases with increasing solids detention time (sludge inventory/sludge wastage rate). However, practical limits exist due to phenomena such as bulking, when the predominance of filamentous bacteria at high solids detention times causes clumping and floating of sludge and difficulties with solids separation.

Many approaches for the design of activated sludge plants have been developed. One set of design equations, for example, which assumes that bacterial growth follows Monod kinetics was developed by McCarty and Lawrence (1970). With these equations, the activated sludge plant volume required to obtain a given reduction in pollutant concentration can be calculated, given the wastewater flow rate, pollutant inlet concentration, kinetic parameters for the pollutant, design microorganism concentration, and solids detention time safety factor. Several design approaches for suspended growth processes are given in Appendix G.

Powdered activated carbon (PAC) is sometimes used to enhance the activated sludge process. This is usually only considered when an existing plant is not performing adequately and process control parameters cannot be further manipulated. Bacteria tend to attach themselves to solid surfaces with extracellular polymers when possible. Activated carbon concentrates organic solutes on its surface. Thus, the activated carbon concentrates both the pollutant and the microorganisms that will degrade the pollutant on its surface. This sometimes results in a reduction in effluent organic concentrations. The price for the incremental removal is the cost of the PAC and in the additional solids handling and disposal costs.

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## 15. Anaerobic Digestion

Anaerobic digestion is the anaerobic counterpart to activated sludge. In this suspended growth, anaerobic biological process, carbon dioxide and methane are the primary products. The same equations that apply to activated sludge apply to anaerobic suspended growth processes, but the values of the constants in the Monod expression are very different (see Appendix G). Growth rates in anaerobic processes are much slower than in aerobic processes, making them much more susceptable to upset due to fluctuations in feed quality or flow conditions. Similarly, recoveries from upsets are much slower.

Because the cell yield is generally lower in anaerobic processes, less sludge is produced than in the activated sludge process (ASP), and the solid waste disposal problem associated with the process is smaller. Anaerobic digesters are often installed along with activated sludge plants to digest the sludge from the ASP for this reason.

## 16. Trickling Filters

Trickling filters are one of many types of fixed biological film reactors. In a trickling filter, rock, gravel, or some other support medium provides a surface on which a biomass can grow. The support medium is contained in a tank equipped with underdrain and irrigation feed systems. The wastewater containing the pollutant is allowed to trickle over the medium and collect at the bottom of the vessel. Recycle of a fraction of the effluent to the trickling filter inlet is common. The water coming into contact with the biomass supplies food for the growing bacteria. If the pollutant concentration in the wastewater to be treated is not sufficient to support growth, a primary substrate and essential trace elements must be added to promote degradation of the pollutant which serves as a secondary substrate.

While most trickling filters are open to the atmosphere and are considered aerobic, the operation can be conducted under an anaerobic atmosphere. Anaerobic conditions can also exist within a biofilm in a trickling filter open to the atmosphere. Food and oxygen utilized by bacteria away from the water-biofilm interface must diffuse through the biofilm closer to the interface. This part of the biofilm could, therefore, deplete the wastewater of oxygen or substrate. The kinetics of biological growth in a biofilm are described in recent literature (e.g., Namkung et al., 1983; Rittmann, 1982; Rittmann and McCarty, 1981).

Sloughing of biomass should be expected in steady-state operations. Thus, filtration of trickling filter effluent may be required to maintain consistently low BOD and COD levels. Appendix H contains some of the design parameters that can be used to predict trickling filter performance.

## 17. Microfiltration, Ultrafiltration, and Reverse Osmosis

Microfiltration, ultrafiltration, and reverse osmosis (RO) are three pressure-driven processes which use membranes to remove various materials from a liquid stream. The primary difference between the three processes is the size of the material retained as liquid is pushed through

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the membrane. Retention size ranges for the three processes are 0.02-10 microns, 0.001-0.02 microns, and less than 0.001 micron, respectively. In microfiltration and ultrafiltration, rejection is usually governed by shape and size, and the osmotic pressure due to the concentration gradient across the membrane is negligible. Operating pressures in these processes are in the 1-100 psi range. Reverse osmosis has higher operating head requirements (100-800 psi) because of smaller membrane pore sizes and osmotic pressure which must be overcome to obtain flow through the membranes.

Although plate and frame units are available, reverse osmosis units of tubular design are more common in industry. In the tubular design, either a hollow fiber (25-250 micron inner diameter) tube bundle or a dual, spiral-wound membrane assembly can be employed.

Major problems associated with membrane processes are related to membrane degradation and fouling. Design considerations include feedwater quality, operating pressure, recovery ratio (ratio of product water to feed), and unit hydraulics. Membrane processes operating at a constant feed pressure suffer a decline in the product flux due to the accumulation of material on the upstream-side of the membranes. Empirical models such as the Merten equation have been developed to predict flux as a function of time.

Membrane processes have been used effectively in the food, pharmaceutical, plastics, water and wastewater, and pulp and paper industries, but operating costs usually exceed those associated with conventional waste treatment processes. Reverse osmosis has, however, been shown to reduce wastewater volumes from metal finishing rinses by more than 99% by separating the water (reused as rinse water) from dissolved metals and cyanides (returned to plating solutions), according to Rozelle et al., (1973). Design equations for reverse osmosis and other membrane processes are presented in Appendix I.

18. Oil/Water Separation

The separation of oil and water has been a long-standing problem in the petroleum industry and is discussed in standard references like the Chemical Engineer's Handbook (Perry and Chilton, 1973). Conventional methods such as gravity settling and dissolved air flotation are effective in obtaining a course oil/water separation, but removal of small droplets which account for haze requires additional treatment.

The design of oil/water separators as developed by the American Petroleum Institute (API) is based on gravity settling of free oil globules larger than 150 microns (Eckenfelder, 1980). One operating advantage of the API separator is its capacity to handle surge volumes. Examples of gravity settlers of various shapes and sizes are available (Perry and Chilton, 1973; Treybal, 1963).

The presence of surface active agents (e.g., organic detergents) hinders coalescence of the dispersed phase (i.e., the oil). This is a particularly serious problem, for example, in washrack operations where detergents, oils, greases, and solvents are present. The wastewater that results can contain dissolved or emulsified organics which flow with the aqueous phase in an oil/water separator. The formation of micelles (small cells of oil surrounded by the surface active agent) often

results in a net charge in the ionic layer surrounding the micelle and a stable suspension of micelles due to electrostatic repulsion between micelles. The phenomenon is similar to that described earlier in the section on Sedimentation/Coagulation. The charge surrounding the micelles depends upon the surfactant type (i.e., cationic or anionic), and the pH and ionic strength of the aqueous solution. Changing the pH of the solution to the "ZPC" value (pH value at which there is no charge on the micelle) may enhance separation of the oil from the water since it would allow coalescence of micelles. However, two associated potential problems that must be considered are (1) the neutralization of the water after separation, and (2) the change in the solubility of the organic phase in water. Laboratory testing of the wastewater to determine the optimum operating pH value would be necessary.

Addition of emulsion breakers to the wastewater can improve oil/water separation, but laboratory testing is also needed. Furthermore, required dosage rates vary with oil concentrations, making the use of emulsion breakers impractical for batch operations. Dissolved air flotation (discussed earlier) is the most widely used physical process for removal of freed oil following demulsification (Tsugita, 1981).

Oil removal from wastewater containing emulsified oils can sometimes be increased by replacing the existing oil/water separator with a coalescer or by passing the aqueous effluent from the oil/water separator through a coalescer prior to discharge. The coalescer is essentially an oil/water separator in which a portion of the vessel is filled with packing. Packing materials vary from corrugated steel to bundles of fibers (Langdon et al., 1972) to beds of mixed metal granules (Fowkes et al., 1970) to carbon (Gosh, 1947). The packing provides a large surface area on which the micelles or oil droplets can adhere and coalesce into larger droplets. The shorter distance required for the micelles to travel to reach a water/solid interface also improves conditions for coalescence.

Centrifuges are sometimes used to break oil/water emulsions. However, centrifugation is best suited for oily sludges and is not generally used to treat dilute oily wastewater (Tsugita, 1981) as would come from an oil/water separator on an Air Force base.

Electrical demulsification is sometimes used to break water-in-oil emulsions (Tsugita, 1981). The process is energy intensive (i.e., high operating costs) and also appears inappropriate for treating oil/water separator effluent.

A broad variety of alternative oil-water separation processes are described by Yehaskel (1979).

The design of a conventional oil/water separator is similar to that of a sedimentation basin (see Appendix C), except that the dispersed phase is oil rather than suspended solids, and that it rises to the air-water interface rather than sinks to the basin floor. Stoke's Law is used to determine the time required for droplets of a prescribed size and density to rise to the air-water interface. The residence time of the wastewater in the separator must be greater than or equal to the time of rise for the droplets. Water must flow beneath an underflow weir which retains the oil phase for removal from the separator.

The design criteria for the processes mentioned above are not as well defined, and must be tailored to the wastewater flow and characteristics in question. For example, in experiments performed on a kerosene and oil-in-water dispersion, Langdon et al. (1972) found that fibrous bed filters having a coalescer fiber density of 11.6 lbs/cu ft failed to remove only 0 to 7 mg of oil/liter at all velocities investigated. However, decreasing the density to 8.7 lbs/cu ft resulted in poor oil removal efficiency. It would not be prudent to expect the same results for a wastewater containing an oil-detergent-water emulsion.

## 19. Air Stripping

In principle, any nonreacting gas can be used to partially remove dissolved volatile materials from the liquid phase. Since air is readily available as a stripping gas, and there are no major adverse consequences associated with evaporating water, air stripping can be a viable treatment option for removal of some volatile organic pollutants. At equilibrium, a trace organic will partition between gas and liquid phases as prescribed by the Henry's law constant for that organic. If the organic solute is not toxic at the gas-phase concentration that would result, it may be sufficient to vent the stripping column directly to the atmosphere. Photochemical processes degrade some organic compounds more rapidly than conventional liquid-phase biological processes, so that air stripping can result in a more rapid degradation of some pollutants under favorable conditions. Toxic solutes that cannot be discharged to the atmosphere can be captured by discharging the stripping column effluent into granular activated carbon beds prior to venting to the atmosphere.

Air-stripping columns used in wastewater treatment typically contain packing rather than conventional distillation column trays. Rates of mass transfer between nonequilibrium gas and liquid phases can be calculated using design equations based on material balances. Process design calculation procedures are outlined by Treybal (1980). For highly volatile solutes, the rate of mass transfer is governed by the resistance to mass transfer in the liquid phase. In general, however, both liquid- and gas-phase resistances to mass transfer should be considered since the gas-phase resistance may be important under certain conditions as shown by Riojas et al. (1983) for chlorinated organics such as 1,1,1-trichloroethane and perchloroethylene.

Steam is sometimes used instead of air in stripping operations because it heats the solution while it provides stripping gas. This raises the vapor pressure of the volatile solute, facilitating its transfer into the gas phase, but the process is generally more energy intensive than air stripping. Detailed mechanical design procedures are presented by Ludwig (1964). Process design equations are included in Appendix J.

## 20. Chemical Reduction

This process is noteworthy because it is one of several processes used to remove chromium from wastewater. However, the chemical principles involved are applicable to any material which becomes insoluble in the reduced state.

Hexavalent chromium in the form of chromate is water-soluble and toxic to aquatic life. Trivalent chromium, on the other hand, precipitates at elevated pH values. Hexavalent chromium is readily reduced by a wide variety of materials including many organic compounds and

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metals (Case, 1974). However, reducing gases such as sulfur dioxide are used most often. Hydrogen sulfide is not used due to its high toxicity, but, in theory, it could be used as a reducing gas as well.

In many commercial reduction operations, sulfur dioxide is used in the reduction of chromium. Because sulfur dioxide hydrolyzes to hydrogen sulfite which readily oxidizes to sulfuric acid, its addition to a wastewater results in a drop in pH. Dropping the pH of the wastewater with sulfuric acid prior to sulfur dioxide addition shifts the sulfur dioxide/sulfuric acid equilibrium away from sulfuric acid formation, making more sulfur dioxide available for chromate reduction and reducing sulfur dioxide feed requirements.

The removal of hexavalent chromium from wastewater proceeds in two steps: reduction and precipitation. Good contact between the water and the gas is important for effective chromate reduction and to avoid the release of sulfur dioxide to the atmosphere. The water and gas are contacted in a mixing chamber where soluble trivalent chromium is formed. The trivalent chromium is then precipitated by raising the pH of the wastewater, usually through lime addition at the mixing chamber outlet, and removed through clarification. The solubility of trivalent chromium is at a minimum near a solution pH of 7. Figure 1, taken from Pourbaix (1966), shows the solubility of chromic oxide ($Cr_2O_3$) and chromic hydroxide ($Cr(OH)_3$) in pure water. These chromium compounds are two of the dominant trivalent chromium species.
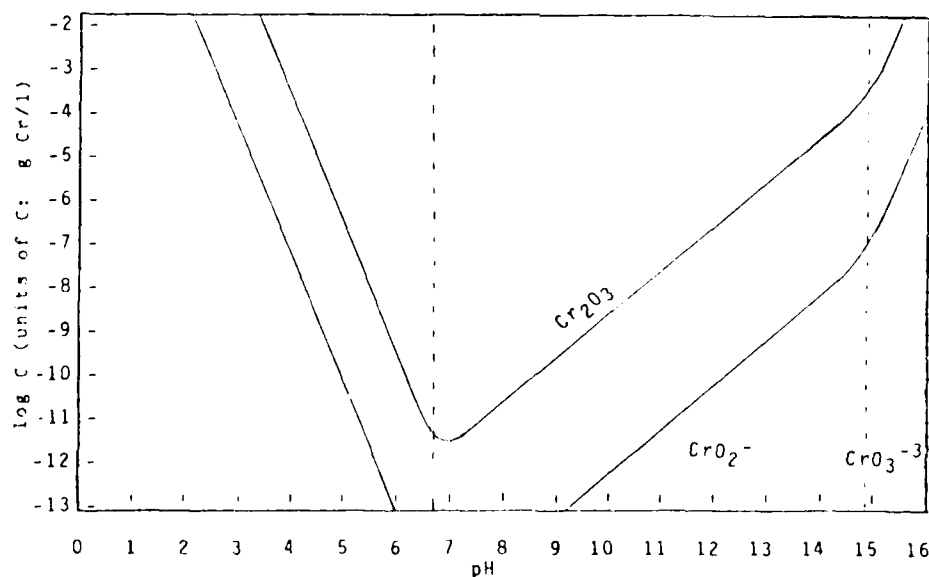


Figure 1. The influence of pH on the solubility of chromic oxide and chromic hydroxide at 25°C.

The precipitate that forms is rich in trivalent chromium and settles to the bottom of the clarifier where it is removed for solid waste disposal. Design considerations are discussed in Appendix D.

D. Utilizing and Combining Wastestreams Prior to Treatment.

There are usually many options available in the selection of a treatment process for a given wastewater stream. Prior to selecting a treatment process, alternatives should be investigated thoroughly. This includes options such as wastewater stream recycle, pollutant recovery (for reuse) from wastewater streams, and wastewater stream utilization in the same or nearby processes. For example, some rinse streams can be recycled for reuse if the pollutant concentration is far from its solubility limit in water. This has been demonstrated in the metal plating industry where as much as 75-80% of the rinse water can be recycled, following a closed-loop chemical wash step which reduces pollutant concentrations in the rinse water (Williams, 1974; Martin, 1973). Other examples include the recycling of washrack wastewater (Chian et al., 1974), the processing of wastestreams containing solvents (say using distillation or steam stripping) to recover the solvents for reuse, and the blending of wastewater streams containing chromate and zinc with feedwater to cooling towers where these metals are added as part of the cooling water treatment. Of course, caution must be exercised to assure that the industrial processes involved are not adversely affected.

If an exhaustive review of feasible non-treatment alternatives produces no resolution of the wastewater problem, potentially appropriate treatment processes can be selected from Table 20. However, to optimize the selection, the requirements of the processes being considered as well as the availability and flow rates of nearby wastewater streams must be kept in mind. For example, metal plating wastewaters are sometimes treated using biological treatment processes. Because these wastewater streams are low in organic matter, addition of a primary substrate and trace nutrients is required. If a second wastewater stream containing a toxic compound (above the inhibitory threshold concentration for a biological treatment process) and a biodegradable organic contaminant is generated nearby, the first wastewater stream could serve to dilute the second so that the concentration of the toxic compound is below the inhibitory concentration while the second wastewater stream would provide substrate needed for the biological treatment of the first stream. By mixing the two wastewater streams, both streams could be treated by a single process which might not have been used to treat either stream alone, and the combined operation might be more efficient than treating the two streams separately. (The sludge generated would, of course, be rich in the metal contaminant.) The final selection of treatment processes should, therefore, be made by someone having an overview of all operations on base and an understanding of the characteristics and requirements of the treatment processes being considered. Economy, safety, and reliability of operation should be the determining factors for any selection.

E. Biotransformation of Total Toxic Organics

The presence of highly chlorinated toxic organics in a wastewater stream creates special treatment problems. Compounds such as carbon tetrachloride, tetrachloroethylene, and 1,1,1-trichloroethane are relatively persistent in the evironment but can be biologically degraded in wastewaters, both aerobically and anaerobically. Under oxidizing conditions, the transformations are very low due to the highly oxidized state of the chlorinated organics. Under anaerobic

conditions, these compounds are transformed by biooxidation or reductive dehalogenation (Bouwer and McCarty, 1983; Vogel and McCarty, 1985; Parsons and Lage, 1985) to compounds which contain less halogen atoms per molecule, are also highly volatile (see Munz and Roberts, 1987, Riojas et al., 1983, or Mackay and Shiu, 1975, for values of some Henry's Law constants), and are often more toxic than the original compounds.

In the four-step anaerobic biodegradation of perchlorethylene, where the products of the four steps are trichloroethylene, dichloroethylene, vinyl chloride and carbon dioxide (Vogel and McCarty, 1985), the intermediate products are included in the list of toxic organics for which there is a limit on the total discharge concentration. Thus, unless mineralization (degradation to carbon dioxide) is insured, no significant decrease in TTO due to chlorinated organics would result from biological treatment of the wastewater.

## III. CONCLUSIONS

All pretreatment processes consume both manpower and financial resources. This does, however, reduce the wastewater treatment burden downstream. Recycling water is often the simplest, most reliable, and cost effective method of reducing pretreatment requirements. Product recovery or substitution of the product used to an unregulated, less toxic product is sometimes possible. Treatment at the wastewater source should always be investigated thoroughly.

Pretreatment processes selected must be capable of meeting current and anticipated pollutant concentration limits. Preferred pretreatment methods are pollutant-specific. That is, a process that is effective in removing one pollutant may not be an effective treatment method for another pollutant. In selecting a pretreatment process, all options should be considered, including the possibility of combining wastewater streams prior to treatment.

Removal efficiencies and typical effluent concentrations for many pollutants and industrial processes are reported in the EPA Treatability Manual Vol. I (USEPA, 1980a) and reproduced in Table 20. However, neither operating conditions nor the form of the pollutant (e.g., oxidation state of chromium) are given. Thus, many factors must be examined before making a process selection.

Operating conditions must be considered in selecting a pretreatment process since removal efficiencies can suffer a sharp decline if conditions are not near optimum. For example, activated sludge may not be appropriate in cold climates since microbial metabolism rates are greatly reduced at low temperatures.

Difficulties may also arise when a wastewater stream contains more than one pollutant. The preferred treatment method for one may not be the preferred method for the other. In fact, one pollutant may hinder the efficiency of a process in the removal of another pollutant. The presence of bacteria, algae, or organics (e.g., humic acids) may also reduce pollutant removal efficiency through temporary or permanent fouling in processes such as ion exchange, activated carbon adsorption, and reverse osmosis.

When selecting a treatment process, the consequences of the process must be considered. For example, a process which converts one pollutant to another (as with the degradation of 1,1,1-trichloroethane) or converts one type of pollution to another (e.g., air stripping a refactory compound in an area with marginal air quality) would not be the appropriate selection.

The quantity and frequency of disposal of waste or spent materials (e.g., waste sludge from activated sludge plants or spent activated carbon) will have a major impact on cost and required operator/maintenance effort.

Process reliability is dependent on the level of training of operations and maintenance personnel. If the required trained personnel are not available to operate and maintain process equipment, a "reliable and efficient" process can be rendered ineffective.

## IV. RECOMMENDATIONS

The selection of pretreatment facilities is necessary when it becomes impossible to meet pretreatment standards or when the POTW experiences operating problems attributable to a particular wastewater stream generated on base. Before considering pretreatment facilities, determine if the condition is a recent development or a long-standing problem. If it has not been a problem in the past, look for what caused the change. Otherwise, look at the process that is generating the wastewater and attempt to resolve the problem through process modification or water reuse.

If pretreatment is indeed needed, determine what process(es) might be used to obtain the required effluent concentration(s) using Table 20. Wastewater treatability studies should be considered as a process-screening tool for all wastewater streams for which little or no treatability data exits. They should also be considered for verifying the efficacy of the pretreatment process selected when the wastewater has an unusual property or characteristic. Apparently small variations in wastewater characteristics can have a profound effect on the performance of a wastewater treatment process. The investment of time and money in laboratory-scale studies can prove invaluable. If there is any question about the treatment of a wastewater stream or process selection, call USAFOEHL for clarification.

Give the tasks of designing and installing any wastewater treatment facility to a reputable architectural and engineering (A & E) firm, once the pretreatment processes have been screened. The final process selection should be made with the benefit of the experience of professionals who may have designed facilities to treat similar wastewater streams. However, the final selection should be made by Air Force personnel, taking into consideration factors such as cost, safety, reliability, process operation complexity, and time required for design and installation. Improper design or installation lead to subsequent problems. To whatever extent possible, the Bioenvironmental Engineer on base should review and understand the design before installation begins, and follow the progress of the installation of the wastewater treatment facility to verify that it conforms to the design. If any questions arise concerning the design of the facilities, contact USAFOEHL before committing funds to the purchase and installation of equipment.

Proper maintenance and operation of the facilities are essential if pollutant concentrations are to be consistently controlled at or below required levels. This will require the dedication of at least one person, part-time, and could demand the attention of several people, full-time, depending on the complexity of the process. It is, therefore, essential that funds and personnel be allocated for the operation and maintenance of the facilities from the pretreatment project's inception. If Air Force personnel are not available for operating and maintaining the equipment, outside contractors should be hired for this purpose.

Finally, a concerted effort should be made to establish a good relationship with the personnel at the POTW that receives the wastewater leaving the Air Force Base. Know their requirements and how Air Force operations affect the performance of the POTW. They can be a great asset in the initial troubleshooting of new wastewater treatment facilities, especially when they know that proper operation of the Air Force facilities will improve the operation of the POTW.

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# APPENDIX A

Design of Gas Flotation Facilities

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# DESIGN OF GAS FLOTATION FACILITIES

In dissolved gas flotation, one of the key parameters for proper operation is the gas-to-solids ratio. Eq. A-1 gives the gas-to-solid ratio as a function of other wastewater or sludge characteristics and operating parameters.

$$G/S = C_g (fP - 1) q/(C_s Q) \qquad (A-1)$$

where $C_g$ = solubility concentration of gas in liquid
$f$ = fraction of air dissolved in pressure tank (0.5-0.8)
$P$ = absolute pressure ratio (pressure tank/flotation tank)
$q$ = volumetric flow rate of portion of feed to flotation
tank being pressurized
$C_s$ = solids concentration
$Q$ = wastewater or sludge volumetric flow rate to unit
$G/S$ = gas/solids ratio.

The gas-to-solid ratio is dimensionless when the concentrations, $C_g$ and $C_s$, and the flow rates, q and Q, have like units. However, it represents a mass ratio rather than a volume ratio.

Typical ranges for important design parameters for dissolved gas flotation as applied to the removal of biological sludges from water with air are given in Table A-1 (Qasim, 1985).

## Table A-1

### DISSOLVED GAS FLOTATION DESIGN PARAMETER RANGES

| Sludge Type | Air/Solids Ratio | Solids Loading Rate (kg/m$^2$.d) | Hydraulic Loading Rate (m/d) | Polymer Dosage(mg/kg) | Removal (%) |
|---|---|---|---|---|---|
| primary | 0.04-0.07 | 90-200 | 90-250 | 1000-4000 | 80-95 |
| WAS* | 0.03-0.05 | 50-90 | 60-180 | 1000-3000 | 80-95 |
| Trickling Filter | 0.02-0.05 | 50-120 | 90-250 | 1000-3000 | 90-98 |
| Primary + WAS* | 0.02-0.05 | 60-150 | 90-250 | 1000-4000 | 90-95 |

*WAS = Waste Activated Sludge

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# APPENDIX B

Design of Filtration Facilities

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# DESIGN OF FILTRATION FACILITIES

The design and performance of a filter for removal of suspended solids from a liquid are related to the filter coefficient, F, which is in turn a function of the collection efficiency of individual granules of the filter medium (collectors). Assuming that solids removal is a first-order process (i.e., removal rate is proportional to suspended solids concentration), the change in the suspended solids concentration with filter bed depth can be shown to be proportional to the suspended solids concentration, with the filter coefficient being the proportionally constant, as shown in the partial differential equation presented in Eq. B-1 (Weber, 1972).

$$\partial C/\partial x = -FC \tag{B-1}$$

where $C$ = suspended solids concentration
$x$ = direction of flow

The filter coefficient is given in Eq. B-2.

$$F = -1.5 \left[(1-\varepsilon)/d_g\right] \eta \, \eta_c \tag{B-2}$$

where $\varepsilon$ = bed porosity = void volume/total volume (a function of deposited solids and, therefore, of time and bed depth)
$d_g$ = grain diameter
$\eta$ = collector efficiency factor = sticking factor
$\eta_c$ = overall single collector efficiency

The collection efficiencies associated with gravity, interception, and diffusion are given in Eqs. B-3, B-4, and B-5, respectively. Eq. B-6 gives the overall collector efficiency as the sum of the three major components listed in the previous three equations.

$$\eta_g = \left[(\rho_s - \rho_l) \, g \, d_p^2\right] / (18 \, \mu \, v) \tag{B-3}$$

$$\eta_i = 1.5 \, (d_p / d_g)^2 \tag{B-4}$$

$$\eta_d = 0.9 \left[kT / (\mu \, d_p \, d_g \, v)\right]^{2/3} \tag{B-5}$$

$$\eta_c = \eta_g + \eta_i + \eta_d \tag{B-6}$$

where $\eta_g$ = collector efficiency due to gravity

$\eta_i$ = collector efficiency due to interception

$\eta_d$ = collector efficiency due to diffusion

$\rho_s$ = density of suspended particle

$\rho_l$ = density of liquid

$g$ = gravitational constant

$d_p$ = diameter of suspended particle

$\mu$ = viscosity

$v$ = approach velocity

$k$ = Boltzman's constant

$T$ = Absolute temperature

The collector efficiency factor, $\eta$, represents the fraction of collisions between suspended particles and filter medium grains that result in deposition on the surface of the grains. Its value is 1.0 in the ideal filter, and approaches 1.0 in filters which are precoated with filter-aid polymers. However, any polymer used in a filtration operation should be tested thoroughly before use because a decrease in backwash efficiency could negate any benefits that might otherwise be achieved.

Eq. B-1 can be integrated numerically to give information such as the suspended solids concentration at the outlet of a bed of specified depth as a function of time, or the bed depth required to reduce suspended solids concentrations to a specified level as a function of time. However, the pressure drop (head loss) across the filter bed and the effluent suspended solids concentration reach their maximum values at the same time in an optimally designed filter.

The Carman-Kozeny equation, given in Eq. B-7, predicts the head loss across a filter bed, $h_L$, as a function of flow condition, medium characteristics, and bed porosity, which changes with time.

$$h_L = |f'/\phi| \, |L/d_g| \, |(1-\epsilon)/\epsilon^3| \, |(Q/A)^2/g| \qquad (B-7)$$

where $f'$ = friction factor for the Carman-Kozeny equation

$\quad = 150 \, (1 - \epsilon)/ Re + 1.75$

$Re$ = Reynolds number = $(\phi \, \rho_l \, d_g \, Q)/(\mu \, A)$

$\phi$ = shape factor (0.73 for coal, 0.82 for angular sand, 0.75 for regular sand)

$L$ = bed length

$Q$ = volumetric flow rate

$A$ = cross-sectional area of the filter bed

Because the porosity of the filter bed varies with depth, the above equation can be used in the form presented only when the filter bed is clean. Otherwise, the head loss across the bed can be estimated by considering thin slices of filter medium, calculating the head loss across each, and summing the head losses obtained. In order to do this, the porosity must be determined by calculating the solids deposition as a function of time and depth.

Darcy's Law, which predicts the flux through a filter under laminar flow condition as a function of its depth, L, the head loss across it, $h_L$, and its permeability, K, is given in Eq. B-8 for the case where the head loss-to-depth ratio is uniform throughout the filter.

$$Q/A = K \, h_L / L \qquad\qquad\qquad (B-8)$$

The Carman-Kozeny equation can be manipulated to reveal the nature of the proportionality "constant," K, in Darcy's Law. In summary, filter performance can be predicted by integrating a partial differential equation (Eq. B-1) over time and over the length of the filter bed. To optimize a filter design, two partial differential equations (the differential forms of Eq. B-1 and Eq. B-7) must be simultaneously integrated over time and the length of the filter, so that the time required to reach the maximum effluent suspended solids concentration and the maximum allowable filter bed head loss both equal a prescribed value, compatible with manpower and capital available for the purchase, operation, and maintenance of the filter bed installation.

Although there is some theoretical basis for the design of filters, most are designed on the basis of experience, with typical values for media size, depth, and filtration rate being 0.4 to 0.5 mm, 2 to 3 ft, and 2 gpm/sq ft, respectively (Donovan, 1970).

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# APPENDIX C

Design Sedimentation/Clarification Facilities

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# DESIGN SEDIMENTATION/CLARIFICATION FACILITIES

Solids removal through sedimentation can be carried out in many types of equipment having very different appearances and bases of operation. The two kinds of sedimentation units which will be considered in this appendix are (1) rectangular, horizontal-flow basins, and (2) circular, solids-contact clarifiers.

## Rectangular, Horizontal Basins

Given the volumetric flow rate, Q, the hydraulic retention time, $t_1$, is related to Q and V, the basin volume, as shown in Eq. C-1.

$$t_1 = V/Q \tag{C-1}$$

where V = W L D,
        W = width of basin
        L = length of basin,
        D = depth of water in basin,

The settling velocity for suspended particles in a liquid can be determined using Stoke's Law given in Eq. C-2.

$$v_s = Kg(d_s)(\rho_s - \rho)/(18\,\mu) \tag{C-2}$$

where $v_s$ = settling velocity,
        g = gravitational constant,
        $d_s$ = diameter of the suspended particle
        $\rho_s$ = density of the suspended particle,
        $\rho$ = density of the liquid,
        $\mu$ = viscosity of the liquid, and
        K = shape factor (for non-spherical particles)

The time for solids to vertically traverse the basin, $t_2$, is the same as the settling time for solids entering at the top of the basin distribution box to reach the bottom and can be calculated using Eq. C-3.

$$t_2 = D/v_s \tag{C-3}$$

The minimum volume required to remove suspended particles of a specific size corresponds to the situation where $t_1$ equals $t_2$. Solids suspended in a liquid are generally distributed over a size range. Thus, the size distribution and required removal efficiency will determine the value of $d_s$ used in Eq. C-2. The overflow rate for the basin (flow/surface area of basin) is obtained by setting the reciprocal of $t_1$ equal to the reciprocal of $t_2$ and canceling D from each side, as shown in Eq. C-4.

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$$Q/(W\,L) = Kg(d_s)^2(\rho_s - \rho)/(18\,\mu) \qquad\qquad (C\text{-}4)$$

A typical range of overflow rates in basins used to treat domestic wastewater is 20 m/d to 80 m/d, and corresponds to solids removal efficiency range of 80% to 40%, respectively (Qasim, 1985).

The above development suggests that overflow rate, and not volume, is the important design parameter. In principle, this is correct; however, for a given overflow rate, small volumes correspond to shallow basins, and violation of implicit assumptions results in basins that are not sufficiently deep. The primary assumptions in the development are related to the use of Stoke's Law which applies to particles falling in laminar flow in a still bulk liquid. The assumption of a still bulk fluid is equivalent to an assumption of plug flow in the horizontal direction and can be relaxed to include laminar horizontal flow. Thus, there is a practical limit with regard to minimum basin depth because of turbulence and viscous effects. Similarly, there is a practical limit as to the minimum width of the basin, corresponding to the width where viscous wall effects become significant. Therefore, the width and depth must be checked to assure laminar flow. In an open channel, this corresponds to values of the Reynolds Number (Re) less than about 500. The Reynolds Number for open channels is defined in Eq. C-5.

$$Re = 4R\nu\rho/\mu = 4(A/P)(Q/A)\rho/\mu = 4Q\rho/P\mu \qquad\qquad (C\text{-}5)$$

where Re = Reynolds Number (dimensionless)
     $R$ = hydraulic radius = $A/P$
     $\nu$ = velocity of liquid
     $\rho$ = density of liquid
     $\mu$ = viscosity of liquid
     $A$ = cross-sectional area
     $Q$ = volumetric flow rate
     $P$ = wetted perimeter

Typical depths for sedimentation basins range from 5 to 16 feet. Thus, the width is selected, based on space restrictions or manufacturer specifications, the length is calculated using Eq. C-4, and the depth is determined using Eq. C-5. The minimum volume (but not necessarily minimum cost) corresponds to the design having the basin width equal to the basin depth.

Horizontal velocities near 1.0 cm/sec and 3.0 cm/sec correspond to optimum efficiency of primary solids removal and maximum design velocity, respectively. Basins are designed with depth-to-length ratios ranging from 1:10 to 1:30, and widths of 6 to 10 meters (Kalbskopf, 1970).

Scrapers and skimmers are in continuous operation to remove settled solids and floating oils and scum respectively. Sizing is specific to the characteristics of the wastewater and the concentrations of solids, oils and greases. However, standard designs usually offer sufficient latitude to preclude operating problems for most wastewaters.

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## Circular, Solids-Contact Clarifiers

Solids-contact clarifiers generally exhibit better hydraulic performance at comparable solids removal efficiencies when compared to horizontal-flow sedimentation basins. These clarifiers have several distinct sections and perform the two major functions of clarification and thickening. The areas required for clarification, $A_c$, and for thickening, $A_t$, can be estimated from Eqs. C-6 and C-7, respectively (Reynolds, 1982). The area to be used in the clarification section is the greater of the two areas.

$$A_c = 2.0 \ Q/V_o \qquad\qquad\qquad (C-6)$$

where $V_o$ = settling velocity of particles which are to be completely removed

$$A_t = 1.5 \ (Q + R) \ t_u/H_o \qquad\qquad\qquad (C-7)$$

where R = sludge recycle rate
$t_u$ = time in a batch settling test required to obtain the design underflow solids concentration
$H_o$ = initial height of sludge in batch test

In Eq. C-6, $V_o$ can be obtained through Stoke's law, but is usually determined experimentally through batch settling tests. The batch test would consist of correlating the concentrated sludge height with time and is represented in Fig. C-1.
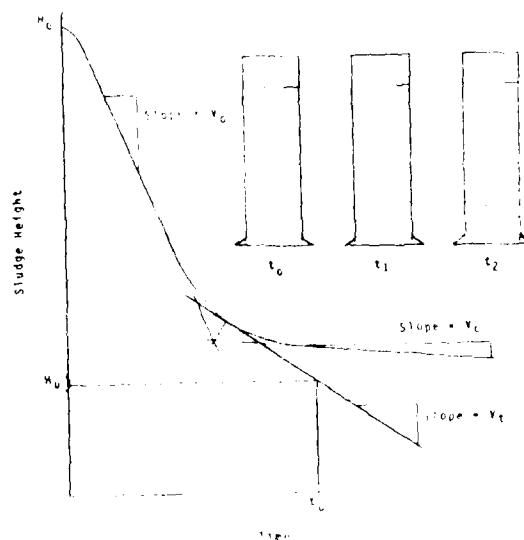


**Figure C-1. Batch settling test and results.**

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The derivative of the sludge height vs time curve represents the sludge settling velocity which, as shown in Fig. C-1, has three distinct regimes. $V_o$ is the sludge settling velocity in the hindered settling zone, that zone in which relatively rapid settling occurs. There is little settling in the compression zone, the zone in which sludge compaction occurs and which has a settling velocity, $V_c$, near zero. Allowing the sludge to remain in the clarifier long enough for compression-zone settling to occur would require large residence times, large clarifier volumes, and consequently high capital investment. Removal of sludge from the bottom of the clarifier results in the formation of a layer of sludge having a relatively uniform solids settling rate greater than $V_c$. The settling rate selected, $V_t$, will determine the residence time, $t_u$, required for the concentration available at the bottom of the clarifier to reach the desired value, as well as the volumetric rate of sludge removal. Thus, the performance of a clarifier can be estimated by following the tangent line to the batch settling curve at the settling rate selected. The value of $V_t$ is determined as indicated in Fig. C-1 in most designs.

The sludge height in the batch test, $H_u$, that corresponds to the design underflow concentration, $C_u$ (e.g., 10,000 mg/l for activated sludge recycle), is obtained by a mass balance as indicated in Eq. C-8.

$$C_o H_o = C_u H_u \qquad\qquad (C\text{-}8)$$

The coefficient values of 1.5 and 2.0 in Eqs. C-6 and C-5, respectively, are scale-up factors to allow for nonideal conditions in the full-scale unit.

If a clarifier is to be used in a process involving chemical reaction (e.g., lime softening or alum coagulation) it provides the additional function of rapid-mixing. However, biological and chemical sludges have different settling characteristics which should be considered when designing a clarifier.

Clarifiers used for chemical treatment sedimentation should have maximum overflow rates (liquid feed rate divided by top surface area, corresponding to minimum clarifier diameter) in the range of 500-600 gal/day-ft$^2$, 700-800 gal/day-ft$^2$, and 1400-1600 gal/day-ft$^2$ for alum, iron salts, and lime treatments, respectively (Reynolds, 1982). The design range for the weir loading in clarifiers using alum and iron salts should not exceed 10,000 to 15,000 gal/day-ft, while the corresponding range for lime sludges is 20,000 to 30,000 gal/day-ft. The average hydraulic detention time for any 24-hour period should be at least two hours (corresponding to the minimum clarifier volume).

Clarifiers used for biological treatment sedimentation should have characteristics listed in Table C-1 (USEPA, 1975).

The most common circular clarifier design incorporates a central feed chamber and a peripheral effluent weir; however, other configurations (e.g., peripheral feed and effluent, peripheral feed and central effluent) are possible. Recent studies suggest that the peripheral feed and central effluent draw-off clarifiers are more efficient in removing solids from some wastewater than are clarifiers having a central feed and peripheral effluent weir (Qasim, 1985).

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## Table C-1

## DESIGN RANGES FOR BIOLOGICAL TREATMENT CLARIFIERS

| Treatment | Overflow Rate* | | Solids Loading* | | Depth |
|---|---|---|---|---|---|
| Process | Average | Peak | Average | Peak | (ft) |
| Activated Sludge (excluding EA**) | 400-800 | 1000-2000 | 20-30 | 50 | 12-15 |
| Activated Sludge (EA**) | 200-400 | 800 | 20-30 | 50 | 12-15 |
| Activated Sludge (pure oxygen) | 400-800 | 1000-2000 | 25-35 | 50 | 12-15 |
| Trickling Filter | 400-600 | 1000-2000 | - | - | 10-12 |

*Units are in gal/day-ft$^2$ and lb/day-ft$^2$ for overflow rate and solids loading, respectively.
**EA = extended aeration

## Inclined Surface Settling

The performance of existing clarifiers or surface area requirements for clarifiers being designed can be improved or decreased, respectively, through the use of suspended inclined surfaces. The inclined surface is usually in the form of multiple-flow-path modules situated near the water-atmosphere interface. By reducing the distance required for a suspended particle to fall (relative to the direction of flow), higher quality effluent can be obtained for a given overflow rate, or higher overflow rates can be accommodated by an existing clarifier (three- to six-fold increase according to Reynolds, 1982). Turbulence is reduced (lower Reynolds number) with the installation of the inclined surface modules, but frequent cleaning is required to avoid restriction of flow through the nodules, higher velocities, turbulence, and solids entrainment.

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APPENDIX D

Design of Chemical Oxidation or Reduction Facilities

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# DESIGN OF CHEMICAL OXIDATION OR REDUCTION FACILITIES

The design and operation of chemical oxidation and chemical reduction units are essentially the same, involving the use of equilibrium and kinetic data for the chemical reaction of concern, and the rate equation appropriate for the type of reactor selected. Equilibrium will dictate the minimum concentration achievable, while kinetics will determine the volumes necessary to obtain equilibrium or near-equilibrium concentrations.

Oxidation and reduction reactions involve the transfer of electrons from the material being oxidized (reducing agent or electron donor) to the material being reduced (oxidizing agent or election acceptor). The equilibrium reached between the oxidized and reduced species of an element depend on the pH and pE (related to the redox potential) of the solution in which the reaction(s) takes place. Hence, accurate pH control and accurate chemical dosage methods are essential for the operation of any unit. Because the optimum equilibrium pH needed for the oxidation or reduction reaction or for possible subsequent precipitation steps are not usually in the pH range suitable for discharge, pH neutralization is the last step in any oxidation or reduction unit. The essential elements of these units are described and examples are given by Hess (1970).

An equilibrium distribution of relevant species is assumed in the design of a redox unit. The conditions at which the reactor must operate are determined by this equilibrium distribution. The dependence of the distribution on pH and pE are obtained from diagrams such as Figure 1 (for chromium) or from equilibrium equations from which such diagrams are derived.

Three types of reactors commonly used in industry are the batch reactor, the plug-flow reactor, and continuously stirred tank reactor (CSTR). These reactors, their characteristics, and the advantages and disadvantages of their use are explained by Levenspeil (1972). The required volume of the reactor vessel(s) depends on the type of reactor selected and the reaction rate.

The CSTR is used, almost exclusively, in commerically available package oxidation and reduction units. The required residence time (and, therefore, reactor volume) can be calculated by knowing the feed concentration, the required effluent concentration, and the rate constant for the reaction. Eq. D-1 is obtained by doing a mass balance on a CSTR where a second-order reaction is taking place. The resulting reactor volume, V, obtained by integrating Eq. D-1 and assuming steady state, is given in Eq. D-2.

$$\text{Change in Inventory} = \text{Consumption due to Reaction} + \text{Feed} - \text{Effluent}$$

$$V \, dC = -k \, C \, C_i \, V \, dt + Q \, C_o \, dt - Q \, C \, dt \qquad (D\text{-}1)$$

$$V = |Q(C_o - C) / (k \, C_i \, C)| \qquad (D\text{-}2)$$

where $C_o$ = concentration of material to be oxidized or reduced
in the feed

$C$ = concentration of material in the reactor and effluent

$C_r$ = concentration of reactant added in the reactor

$Q$ = feed volumetric flow rate

$V$ = reactor volume

$k$ = first-order rate constant for the reaction

Most oxidation and reduction processes involve many species and several reactions. If there are several reaction steps in the conversion of reactants to the desired products, the reaction rate constant for the overall reaction can sometimes be assumed to be approximately equal to the reaction rate constant of the slowest step if it is significantly slower than the other steps in the sequence. Reaction rate constants can often be obtained from the literature. If several of the steps are of comparable speed or if the reaction is not second-order, Eq. D-2 does not apply. Expressions for the reactor volume needed for a single higher-order reaction can be obtained by substituting the appropriate reaction rate expression in Eq. D-1, integrating, and solving for V. However, many complicated processes can be approximated by second-order kinetics. If second-order kinetics are to be used to approximate the behavior of a process, batch experiments can be conducted to determine a rate "constant," even though the value obtained may be constant over a limited range of concentrations and does not represent the reaction rate constant for a single reaction.

Since reaction rates are temperature sensitive, designs should be based on the minimum operating temperature anticipated.

# APPENDIX E

Design of Granular Activated Carbon Adsorption Units

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# DESIGN OF GRANULAR ACTIVATED CARBON ADSORPTION UNITS

The design of a granular activated carbon (GAC) bed requires equilibrium and kinetic data relating adsorbed and soluble species. This information comes in the forms of equilibrium isotherms and column-study breakthrough curves.

Eqs. E-1, E-2, and E-3 give the Freundlich, Langmiur, and BET isotherms, respectively, the mathematical expressions most commonly used to describe adsorption data.

$$q = aC^{1/n} \tag{E-1}$$

$$q/Q = bC/(1 + bC) \tag{E-2}$$

$$q/Q = BC/\{(C_s - C)[1 + (B-1)(C/C_s)]\} \tag{E-3}$$

where  $q$ = sorbed concentration (g/g carbon)
$Q$ = monolayer adsorption concentration (g/g carbon)
$b$ = fitting parameter (a function of sorbent, solvent temperature, etc.
$C$ = liquid concentration (g/g water).
$C_s$ = saturation concentration in the liquid
$a, n, B$  = fitting parameters.

The selection of the appropriate carbon is made easier through adsorption isotherm comparison. An upper limit for the carbon bed adsorption capacity is readily obtained, knowing the concentration of the contaminant to be removed from the feed water and the adsorption isotherm. However, equilibrium will not be reached throughout the entire column before reaching the maximum allowable contaminant concentration at the bed discharge.

Adsorption rates are reflected in the characteristic S-shaped breakthrough curves. The sharpness of the curve is a function of column hydraulics. Liquid loadings of 4 to 10 gpm/sq ft and height-to-diameter ratios between 3:1 and 5:1 are commonly used in fixed-bed columns (Reynolds, 1982). The design bed volume can be obtained by dividing the required adsorbent mass by its density. The adsorbent mass can be estimated from breakthrough and equilibrium data and total throughput volume and effluent concentration requirements using Eq. E-4 (Reynolds, 1982).

$$\ln[(C_o/C) - 1] = (k_1/Q)(q_o M - C_o V) \tag{E-4}$$

where $C_o$ = feed concentration

$C$ = effluent concentration

$Q$ = flow rate

$V$ = throughput volume

$M$ = mass of adsorbent

$q_o$ = maximum adsorbed concentration (obtained from equilibrium isotherm)

$k_1$ = rate constant (obtained by taking the slope of the $\ln[(C_o/C) - 1]$ vs. $V$ plot, and multiplying by $Q/C_o$. Note that if the value of $k_1$ is obtained from a breakthrough curve feed rate in bed volumes per unit time should be the same for the column study and the full-scale unit.)

More complex numerical models have been developed (e.g., Thacker et al., 1984) which include the effect of multiple adsorbates, variable feed concentration, etc., in the prediction of column performance.

The head loss across an activated carbon bed can be predicted using Eq. B-7 or B-8, given in Appendix B.

Biological activity on activated carbon can enhance or hinder bed performance, depending on the type of material the bed is intended to remove. For example, if an activated carbon bed is to be used to remove biodegradable organics which are contributing to a high COD problem, bacteria growing on the GAC may enhance the reduction of COD by degrading organics in the water and on the surface of the carbon medium, thereby reducing the COD/activated carbon ratio. However, they may contribute to fouling problems. Designs should not include possible enhance performance due to biological growth. The effect of biodegradation within the GAC bed should be evaluated on an individual basis.

Ranges for design parameters normally considered are given in Table E-1 (USEPA, 1973).

## Table E-1

## DESIGN PARAMETER RANGES FOR GAC ADSORPTION

| Parameter | Range or Remark |
|---|---|
| Carbon/Waste Ratio | |
|     Tertiary treatment | 200-400 lb/million gal wastewater |
|     Physical-chemical process | 500-1000 lb/million gal wastewater |
| Hydraulic Loading | 2-10 gpm/sq ft |
| Empty Bed Contact Time | 10-50 min |
| Backwash Rate | 15-20 gpm/sq ft |
| Contactor Configuration | gravity or pressure vessel<br>steel or concrete construction |
| Flow Configuration | downflow or upflow<br>single- or multi-stage |

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# APPENDIX F

Design of Ion Exchange Units

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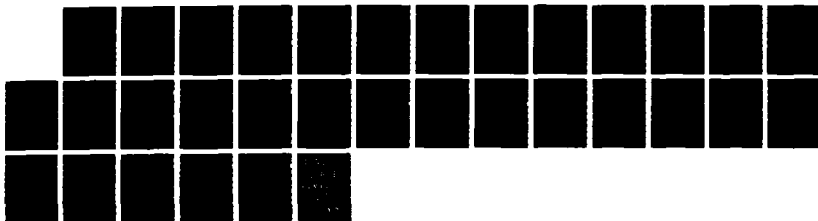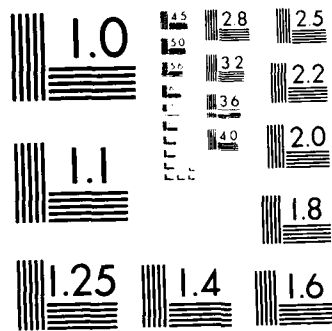
# DESIGN OF ION EXCHANGE UNITS

The design of an ion exchange unit involves the calculation of a resin bed volume needed to produce a prescribed maximum effluent concentration for a desired time period. This time period is called the service cycle of the bed and is related to the time between the required regeneration of a resin bed or resin bed train. To provide for continuous operation of the exchange operation, a minimum of two parallel trains is required. A higher number of parallel trains is commonly installed to increase reliability and reserve capacity of the unit.

The hydraulic characteristics of the resin bed (pressure drop in the downflow mode, percent bed expansion in the upflow mode) are resin-specific. Graphical data are usually supplied by the manufacturer. Figs. F-1 and F-2 are given to illustrate the format in which the data are usually presented.

The volume of the resin bed is determined by the total exchange capacity required of the bed. The total exchange capacity required, $C_t$, is calculated from the liquid flow rate, $Q$, inlet and outlet concentrations, $C_i$ and $C_o$, respectively, and the service cycle time (time to exhaustion), $t_c$, as shown in Eq. F-1.

$$C_t = (Q)\,(t_c)\,(C_i - C_{mo}) \qquad\qquad (F-1)$$
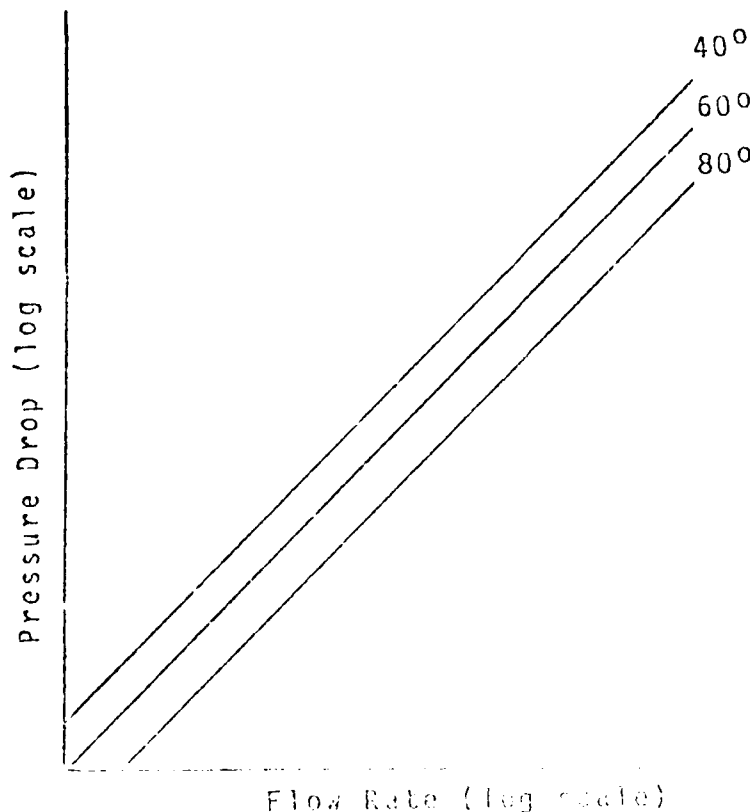


Figure F-1. Resin bed pressure drop data.
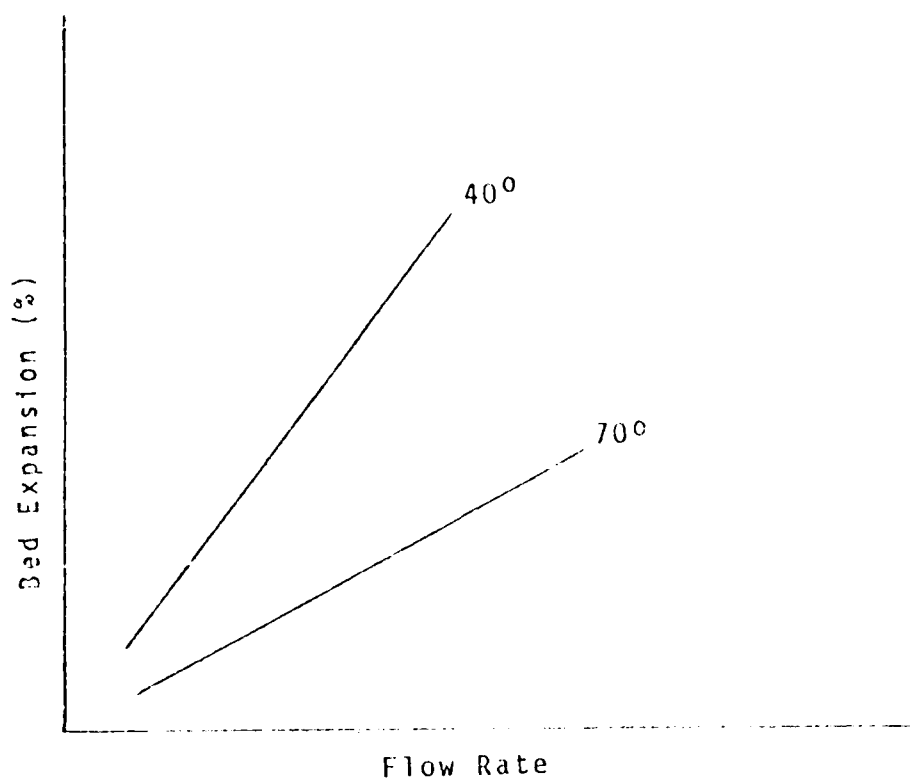
**Figure F-2. Resin bed hydraulic expansion data.**

where $C_{mo}$ is the mean outlet concentration during the service cycle, and Q and $C_i$ are assumed to be constant.

The bed volume is determined from Eq. F-2 which relates the total exchange capacity to the bed volume, $V_b$, and C, the specific exchange capacity of the resin (e.g., gr/cu ft).

$$C_t = (U)(V_b)(C) \qquad\qquad (F-2)$$

where U is the dimensionless resin utilization factor, typically taking a value of 0.9. The value of the utilization factor, in conjunction with laboratory data establishing the condition of the resin, can provide insight into problems at an existing installation which is not performing as designed.

The specific exchange capacity of the resin is a function of the type of resin, efficiency and extent of regeneration, and presence of other materials in solution. These data are usually obtained from the manufacturer. If the application is unique and the manufacturer does not have information on the resin behavior for the application, laboratory studies should be conducted prior to investing in the ion exchange unit installation. Specific exchange capacity data are sometimes given in the form of an equation (equilibrium isotherm) or tabular form by the manufacturer, but the data are usually given in a format similar to that presented in Fig. F-3.
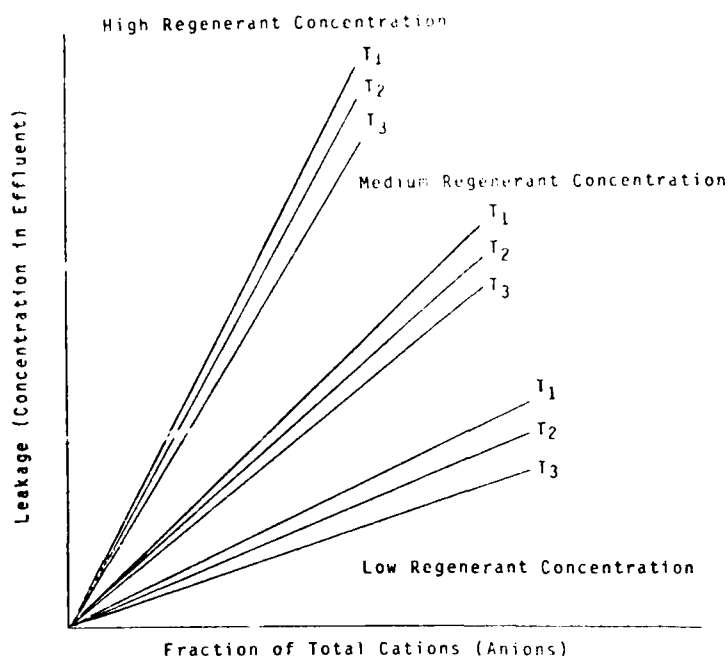
Figure F-3. Specific exchange capacity data.

The required cross-sectional area of the bed is determined from the liquid feed rate and the specific flow rate, q, selected for the design, as shown in Eq. F-3.

$$A = Q/q \qquad\qquad (F-3)$$

The specific flow rate selected for the design should be within the normal operating limits prescribed by the manufacturer for the resin used. An excessively high specific flow rate causes elongation of the saturation front as it proceeds down the bed, resulting in poor utilization of the resin available for ion exchange, while too low a specific flow rate results in poor effluent quality due to problems such as reversal of exchange reactions, maldistribution and channeling. Typical values for design parameters, including a typical range for the specific flow rate, are given in Table F-1 at the end of this appendix.

The bed height is obtained by dividing the bed volume by the area obtained in Eq. F-3. The calculated bed height should be compared with the minimum and maximum bed heights provided by the manufacturer. (See Table F-1 for typical values.) If the calculated value is not within the required range, adjustments must be made (e.g., in the number of parallel trains) so that the bed height can be brought into range.

Vessel dimensions, based on resin bed requirements, can now be determined. (See Table F-1 for typical design parameter values.)

Regeneration facilities and resin vessel features are an integral part of any ion exchange unit design. The following features should be included:

1. Adequate freeboard volume for resin bed expansion during backwash operations (75% of the bed volume is typical).

2. Sight glasses to permit visible verification of the bed level during normal operation and the expanded bed level during backwashing.

3. Air injection spargers to break up the bed at the beginning of the regeneration sequence. (This is particularly important in beds that are used to treat water having silt or biological growth. Loss of substantial portions of the bed can otherwise occur during backwash if the bed cakes up during operation.)

4. Appropriate resin support and effluent collection system (e.g., perforated false bottom, radial collection "spider" with stainless steel screen sleeves, collection piping surrounded by treated quartz gravel underbed).

5. In cation beds which exchange substantial amounts of calcium and are regenerated with sulfuric acid, two step regeneration should be required. The first step should be dilute acid regeneration, followed by a higher acid concentration in the second acid regeneration step. The solubility of calcium sulfate is relatively low, and high solution concentrations of sulfate (from the acid) and calcium (released by the resin) can cause serious blockage in piping and fouling of resin.

## Table F-1

### TYPICAL ION EXCHANGE RESIN BED PARAMETERS

| Parameter | Value |
|---|---|
| Minimum bed height | 2 ft |
| Maximum bed height | 5 ft |
| Freeboard | 75% of resin bed depth |
| Bed diameter | 1-11 ft |
| Service flow rate | 3-8 gpm/sq ft bed area |
| Backwash flow rate | 2-5 gpm/sq ft bed area* |
| Rinse volume | 30-75 gal/cu ft |
| Bed expansion during backwash | 50-75% |

*Varies with desired bed expansion, type of ions on resin, and water temperature

APPENDIX G

Design of Suspended Growth Treatment Facilities

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# DESIGN OF SUSPENDED GROWTH TREATMENT FACILITIES

The design of suspended growth treatment facilities entails the determination of the reactor volume, V, and nutrient requirements for microorganism growth. Knowledge about the feed and kinetic parameters (e.g., bacterial growth and decay constants) that are particular to the type of process being designed are required. Values are obtained from publications or determined experimentally in the laboratory. Design parameters, based on proven operating ranges, are set at the onset of the design.

There are many approaches that are currently used to design suspended growth waste treatment systems. One of the most general is that developed by McCarty (1970). It requires the following information about the feed:

1. Total suspended solids concentration (TSS in feed = $X_o$),
2. Volatile suspended solids concentration (VSS in feed = $X_{V_o}$),
3. Biodegradable fraction of the VSS,
4. Total $BOD_5$ (volatile plus suspended),
5. BOD reaction rate constant ($K_1$),
6. Ammonia-nitrogen concentration.

Kinetic parameter needed for the design include:

1. Maximum utilization rate ($k$),
2. Culture decay coefficient ($b$),
3. Monod half-velocity constant ($K_s$),
4. Substrate fraction used for energy production at zero solids retention time ($a_e$).

In addition, the wastewater feed must be characterized so that an electron donor reaction can be determined, and the electron acceptor must be prescribed.

System design parameters needed for the design include:

1. Mixed liquor volatile solids concentration ($X_V$ or MLVS).
2. Volatile solids concentration in the recycle ($X_{V_r}$).
3. Suspended solids removal in primary treatment.
4. Volatile suspended solids in the effluent from secondary treatment ($X_{V_e}$).
5. Wastewater flow rate ($Q_o$).
6. Safety factor (SF)

The design procedure and equations are given below:

1. Determine the ultimate biochemical oxygen demand, $BOD_l$, for the total waste, and its soluble and solid components.

$$BOD_{L,o} = BOD_5/(1 - \exp\{-5 K_1\})$$

2. Determine the $BOD_L$ of the primary clarifier effluent (feed to the suspended growth unit).

Total $BOD_L$ = soluble + suspended

3. Determine the overall balanced reaction for the wastewater at a solids retention time of zero.

$f_s$, the fraction of the substrate used for cell synthesis, and $f_e$, the fraction of the substrate used for microorganism energy requirements, are functions of the solids retention time, $\theta_c$. ($a_e$ equals $f_s$ at zero solids retention time.)

$$f_e = 1 - f_s$$

The overall reaction is determined by subtracting $f_s$ times the cell synthesis reaction and $f_e$ times the reaction for the electron acceptor from the reaction for the electron donor. In other words,

$$R = R_d - f_s R_c - f_e R_a$$

where  R = overall reaction
$R_d$ = reaction for the electron donor
$R_c$ = reaction for cell synthesis
$R_a$ = reaction for the electron acceptor

4. Determine the cell yield coefficient, Y.

$$Y = C_m M / B$$

where $C_m$ = coefficient of microorganisms from balanced reaction
M = molecular weight of microorganisms ($C_5H_7O_2N$) = 113 g/mole
B = ratio of grams of BOD consumed to moles of electrons transferred
= 8 grams BOD/mole electrons

5. Determine the limiting minimum value for the solids retention time, $[\theta_{c\,m}]_{lim}$.

$$[\theta_{c\,m}]_{lim} = 1 / | Y k - K_s |$$

6. Determine the design solids retention time, $\theta_{cd}$.

$$\theta_{cd} = (SF) [\theta_{cm}]_{lim}$$

7. Determine $f_s$ and $f_e$ at the design value of $\theta_c$.

$$f_s = a_e [ 1 - (f_d \, b \, \theta_{cd})/(1 + b \, \theta_{cd}) ]$$

where $f_d$, the degradable fraction of the microorganisms, is approximately 0.8.

$$f_e = 1 - f_s$$

8. Determine the overall balanced reaction for the wastewater at the design solids retention time.

The overall reaction is determined as in part 3 above, using the values of $f_s$ and $f_e$ found in part 7.

9. Determine the biological solids production rate and solids disposal requirements (production minus effluent). This is done by multiplying the ratio of the substrate reduction to the substrate coefficient (from reaction determined in step 8), by the coefficient for the microorganisms. In other words,

Solids production rate = $[(S_o - S_e)/ C_s](C_m)$

Solids disposal rate = Solids production rate - $Q \, X_e$

10. Determine the effluent substrate concentration, $S_e$.

(It equals the substrate concentration in the water/sludge mixture exiting the reactor.)

$$S_e = S = [K_s \, (1 + k_d\theta_c)] / [\theta_c(Yk - b) - 1]$$

11. Determine the electron acceptor (e.g., oxygen) requirements. This is done by multiplying the ratio of the substrate reduction to the substrate coefficient (from reaction determined in step 8), by the coefficient for the electron acceptor.

12. Determine the liquid residence time and reactor volume.

$$\theta = (\theta_c/X_v)[X_{ro} + (S_e/S_o)X_{do} + Y(S_o - S_e)(1 + f_d \, b\theta_c)/(1 + b\theta c)]$$

$$V = \theta \, Q$$

13. Determine nitrogen requirements or nitrogen concentration in the effluent. If the nitrogen in the feed is less than that required for microorganism production, then nitrogen addition is necessary. If the nitrogen in the feed is more than that required, then excess nitrogen will result in the effluent. The nitrogen requirement is determined by multiplying the ratio of the substrate

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reduction to the substrate coefficient (from reaction determined in step 8), by the coefficient for the nitrogen source (e.g., ammonia).

$$N = [(S_o - S_e)/C_s](C_n)$$

where N = nitrogen requirement
$C_n$ = nitrogen source coefficient

14. Determine sludge recycle requirements (R = recycle ratio = volume of sludge recycled / volume of wastewater treated). This is obtained by doing a mass balance around the clarifier.

$$(Q_o + RQ_o)(X_V) = (Q_e - Q_w)(X_{Ve}) + (RQ_o + Q_w)(X_{Vr}),$$ recalling that $Q_w$ can be obtained from the sludge disposal requirements.

15. Determine the $BOD_5$ in the effluent and compare with requirements.

Alternative design methods, such as that described by Thomson (1975), are available and utilize data from operating plants.

Typical ranges for parameter important in activated sludge plant design are given in Table G-1 (Miorin et al., 1977).

## Table G-1

## SINGLE-STAGE ACTIVATED SLUDGE DESIGN AND OPERATING PARAMETER RANGES

| Process*: | EA | Con | HR | MA | Nit |
|---|---|---|---|---|---|
| _Parameter**_ | | | | | |
| F/M (g $BOD_5$ /g MLSS•d) | <0.05 | 0.15-0.4 | 0.4-1.0 | 1.5-3.0 | 0.05-0.15 |
| $\theta_c$ (days) | >30 | 4-8 | 2-4 | >1 | 10-15 |
| Volume Loading (lb $BOD_5$ /$10^3$ $ft^3$•d) | 10-15 | 20-60 | 70-180 | 90-180 | 10-30 |
| $BOD_5$ Removal (%) | 90+ | 90-95 | 85-90 | 60-75 | 95+ |
| MLSS (g/l) | 2-6 | 1.5-4 | 3-5 | 0.5-1.5 | 3-6 |
| $O_2$ Required (g/g $BOD_5$ Removed) | 1.4-1.6# | 0.8-1.1# | 0.7-0.9 | 0.4-0.6 | 1.1-1.5 |
| $O_2$ Uptake (mg/g MLSS•h) | 3-8 | 7-15 | 15-25 | 20-40 | 3-8 |
| R/Q (-) | 1-3 | 0.3-1 | 0.3-1 | 0.1-0.3 | 0.3-1 |
| Sludge Production (g/g $BOD_5$ Removed) | 0.15-0.3 | 0.4-0.6 | 0.5-0.7 | 0.8-1.2 | 0.15-0.3 |
| V/Q (h) | 16-24 | 4-8 | 2-4 | 0.5-2 | 6-12 |

* EA = Extended Aeration, Con = Conventional, HR = High Rate, MA = Modified Aeration, Nit = Nitrification

**F/M = Food-to-microorganism ratio, MLSS = Mixed Liquor Suspended Solids ($X_v$ is approximately equal to 0.8 MLSS), V/Q = Hydraulic Detention Time in Aeration Basin

# Excluding requirements for nitrification

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APPENDIX H

Design of Trickling Filters

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# DESIGN OF TRICKLING FILTERS

Table H-1 contains a portion of the design information on different types of trickling filters as described by Qasim (1985).

## Table H-1

## TYPICAL DESIGN PARAMETER VALUES FOR TRICKLING FILTERS

| Parameter          Filter Rate: | Low | Intermediate | High |
|---|---|---|---|
| Operation | Intermittent | Continuous | Continuous |
| Recirculation Ratio | 0 | 0-1.0 | 0-2.5 |
| Depth (m) | 1.5-3.0 | 1.25-2.5 | 1.0-2.0 |
| Hydraulic loading (m/d) | 1-4 | 4-10 | 10-40 |
| $BOD_5$ Loading (kg/m$^3$·d) | 0.08-0.32 | 0.24-0.48 | 0.32-1.0 |
| Filter Flies | Many | Medium | Small |
| Power (kW/1000 m$^3$) | 2-4 | 2-8 | 6-10 |
| $BOD_5$ Removal Efficiency (%) | 74-80 | 80-85 | 80-85 |

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APPENDIX I

Design of Membrane Processes

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# DESIGN OF MEMBRANE PROCESSES

The flux of water across a membrane can be described by a typical potential-flux equation, but the form of the equation is slightly different depending upon the water being filtered and the characteristics of the materials being accumulated on the upstream side of the membrane. In its most general form, the equation includes the osmotic pressure difference and resistance to flow due to accumulated material on the upstream side of the membrane, as shown in Eq. 1-1.

$$J = (\Delta P - \Delta p) / (R_m + R_c) \qquad (1\text{-}1)$$

where J = water flux across the membrane = Q/A
  $\Delta P$ = feed pressure minus product pressure
  $\Delta p$ = osmotic pressure of the feedwater minus osmotic pressure of product water
  $R_m$ = resistance to flow due to membrane
  $R_c$ = resistance to flow due to accumulating slime cake (colloidal and suspended solids
    plus biological growth)

For reverse osmosis operations, where the dissolved solids are to be accumulated on one side of the membrane and the water being treated is otherwise relatively free of colloidal and suspended matter, the water flux across the membrane is given in Eq. 1-2.

$$J = (\Delta P - \Delta p) / R_m \qquad (1\text{-}2)$$

For microfiltration processes, where colloidal matter and suspended solids rather than dissolved solids are to be retained on one side of the membrane, the osmotic pressure difference across the membrane is negligible, while the pressure drop across the cake, $R_c$, becomes significant. For this case, the equation that describes the flux of water through the membrane is given by Eq. 1-3.

$$J = \Delta P/(R_m + R_c) \qquad (1\text{-}3)$$

The osmotic pressure of a solution, p, is given in Eq. 1-4 (Reynolds, 1982).

$$p = f \, v \, C \, R \, T \qquad (1\text{-}4)$$

where f = osmotic coefficient (depends on nature and concentration of solute; approximately
     0.0113 psi/(mg/l) for NaCl)
  v = ions/molecule of electrolyte
  C = molar concentration of electrolyte
  R = universal gas constant
  T = absolute temperature

In reverse osmosis operations where the recovery ratio (permeate to feed ratio) is high, a layer of dissolved material can accumulate in a layer on the upstream side of the membrane, providing additional resistance to flow and altering the osmotic pressure difference across the membrane.

Consequently, Eq. I-1 would have to be modified to include the additional resistance. The osmotic pressure difference term would not change but would represent the sum of the osmotic pressure differences across the membrane and the accumulate layer.

The design of a membrane process involves the calculation of the area required to provide a specified product liquid flow for a specified time before requiring maintenance or replacement. The area required is a function of the recovery ratio, pressure drop across the membrane, type of membrane selected, and nature of the wastewater and fouling layer. Fouling is the primary reason for decrease in permeate flow with time required membrane replacement. Many fouling models have been developed for different types of water. Eq. I-5 is given as an example:

$$R_c = \alpha \, w \, V \, (\Delta P)^s \mu / A \qquad\qquad (I-5)$$

where $\alpha$ = constant dependent on properties of fouling layer
$w$ = concentration (wt. basis)
$V$ = volume of filtrate
$s$ = compressibility factor of the fouling layer
$\Delta P$ = pressure drop across the membrane
$\mu$ = viscosity of liquid
$A$ = membrane surface area.

This expression would be substituted into Eq. I-3 yielding an equation which contains both the flux and its integral. Note that the volume of permeate equals the product of the area and the integral of the flux with respect to time. That is,

$$V_p = A \int J \, dt$$

where $V_p$ = volume of permeate.

The area can be determined by numerical means through iteration as described in the steps below, given the minimum volume of filtrate, $V_{min}$, which must be produced in a prescribed time period, $t_p$:

Step 1    Guess required surface area, A

Step 2    Select time increment, dt

Step 3    Set cummulative volume of permeate to zero

Step 4    Set cummulative time to zero

Step 5    Add dt to the cummulative time and compare to $t_p$. If the cummulative time is greater than $t_p$, then return to Step 1 with a larger guess for A.

Step 6    Calculate the volume of permeate (J A dt) generated in the time period using the most recently calculated value of J (use the flux for clean water, supplied by the manufacturer, $J_o$, for first time period).

Step 7    Add the permeate volume obtained in Step 6 to the cummulative permeate volume and compare to $V_{min}$. If cummulative permeate volume is greater than or equal to $V_{min}$ and the difference between $t_p$ and the cummulative time is less than dt, then the last value of A used is the correct value for the design. If the cummulative permeate volume is greater than or equal to $V_{min}$ and the difference between $t_p$ and the cummulative time is greater than dt, then return to Step 1 with a smaller guess for A.

Step 8    Calculate $R_c$

Step 9    Calculate J

Step 10   Go to Step 5

Although the fouling model appropriate for different processes may vary, the general approach would be the same.

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# APPENDIX J

Design of Air Stripping Columns

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# DESIGN OF AIR STRIPPING COLUMNS

The design equations commonly used to design air stripping columns are based on a differential mass balance on a "slice" of the column packing within a stripping column as depicted in Figure J-1. (See Riojas et al., 1983.)

**Figure J-1. Differential mass balance on stripping column.**
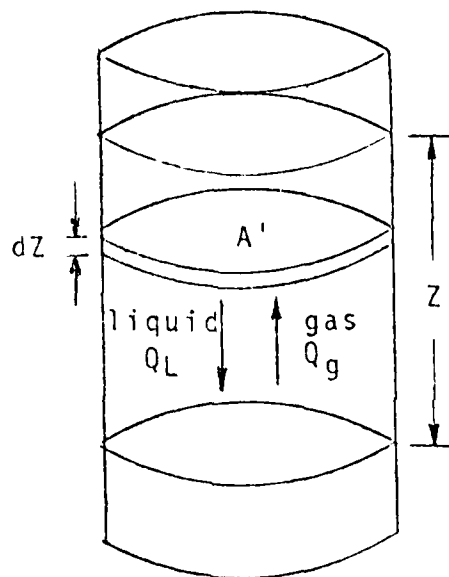
Eq. J-1 represents a mass balance based on bulk-liquid concentrations.

$$\frac{dm_A}{dt} = K_L(A'dz)a\left(c_A^{L*} - c_{AB}^{L}\right) = d\left(Q_L c_{AB}^{L}\right) \tag{1}$$

where $m_A$ = mass of solute A transferred, $t$ = time, $K_L$ = overall mass transfer coefficient based on liquid concentrations, $A'$ = column cross-sectional area, $dz$ = differential column height, $a$ = packing specific surface area, $c_A^{L*}$ = liquid solute concentration that would be in equilibrium with the gas phase, $c_{AB}^{L}$ = bulk liquid solute concentration, and $Q_L$ = liquid volumetric flow rate.

Eq. J-2, the integrated form of Eq. J-1, defines the height of a transfer unit (HTU) and the number of transfer units (NTU). Because the mass balance is based on overall bulk-liquid concentrations, HTU and NTU are often designated as $H_{OL}$ and $N_{OL}$, respectively.

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$$z = \frac{L_M}{\rho_L k_L a} \int_{c_2^L}^{c_1^L} \frac{dc_{A\delta}^L}{(c_A^{L*} - c_{A\delta}^L)} = (H_{OL})(N_{OL})$$ (2)

The integration of the expression for $N_{OL}$, incorporating the simplifying assumption of dilute concentrations, yields Eq. J-3.

$$N_{OL} = \frac{\ln\left[\left(\frac{c_2^L - c_1^G/H_c}{c_1^L - c_1^G/H_c}\right)(1 - A) + A\right]}{1 - A}$$ (3)

where $\rho_L$ = liquid solvent density, $L_M$ = liquid mass flux, $Z$ = total column height, A = absorption factor $= Q_L/H_c Q_G$, $Q_G$ = gas volumetric flow rate, $H_c$ = Henry's constant (mass concentration ratio), and subscripts 1 and 2 designate the bottom and top of the column, respectively.

Thus, $N_{OL}$ is a function of flow rates, solute and solvent properties, and inlet and required outlet concentrations. $H_{OL}$ is a function of the liquid flow rate, packing and liquid properties, and the overall liquid mass transfer coefficient, $K_L$, which can be thought of as the reciprocal of the resistance to mass transfer between the liquid and gas phases. The total resistance to mass transfer is due to the individual resistances in the liquid and gas phases as indicated in Eqs. J-4 and J-5.

$$R_T = R_L + R_G$$ (4)

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_c \cdot k_G}$$ (5)

where $R_T$, $R_L$, and $R_G$ are the total, liquid-phase, and gas-phase resistances to mass transfer, respectively, and $k_L$ and $k_G$ are the liquid-phase and gas-phase mass transfer coefficients, respectively.

In many cases, the resistance in either the liquid- or gas-phase can be neglected. Many correlations have been developed to estimate mass transfer coefficients. One such set of correlations is that of Onda et al. (1968) and is presented in Eqs. J-6 through J-8.

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$$k_L \left(\frac{\rho_L}{\mu_L g}\right)^{1/3} = 0.0051 \left(\frac{L_M}{a_w \mu_L}\right)^{2/3} \left(\frac{\mu_L}{\rho_L D_L}\right)^{-0.5} (a_t d_p)^{0.4} \qquad (6)$$

$$\frac{a_w}{a_t} = 1 - \exp\left[-1.45 \left(\frac{\sigma_c}{\sigma}\right)^{0.75} \left(\frac{L_M}{a_t \mu_L}\right)^{0.1} \left(\frac{L_M^2 a_t}{\rho_L^2 g}\right)^{-0.05} \left(\frac{L_M^2}{\rho_L \sigma a_t}\right)^{0.2}\right] \qquad (7)$$

$$\frac{k_G}{a_t D_G} = 5.23 \left(\frac{G_M}{a_t \mu_G}\right)^{0.7} \left(\frac{\mu_G}{\rho_G D_G}\right)^{1/3} (a_t d_p)^{-2.0} \qquad (8)$$

where $d_p$ = nominal packing diameter, $a_t$ = total packing surface area per bed volume, $g$ = gravitational acceleration, and $\sigma_c$ = critical surface tension (a function of materials of construction of packing and given in Table J-1).

## Table J-1

## CRITICAL SURFACE TENSION FOR VARIOUS PACKING MATERIALS

| Material | $\sigma_c$ [kg/s$^2$] |
|---|---|
| Carbon | 0.056 |
| Ceramic | 0.061 |
| Glass | 0.073 |
| Polyethylene | 0.033 |
| PVC | 0.040 |

The Henry's constant, which appears in the expressions for both the height of a transfer unit and the number of transfer units, is a function of temperature as well as high concentrations of other substances in the wastewater (cosolvent effect). These effects can be pronounced, as discussed by Munz and Roberts (1987).

The process design, thus, is obtained by determining the packed column height (Eq. J-2) necessary to give the desired outlet concentrations, given the type of packing, column dimensions, and fluid flow rates. The mechanical design is based on fluid flow rates, pressure drop considerations, available space, etc. The optimum design is the most economical design (considering both capital investment and operating cost) which meets the problem constraints (e.g., space, effluent concentration) and is obtained through iterative redesign of the unit, varying problem parameters (e.g., flow rates, column diameter).

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